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Locating and Estimating Air Emissions from Sources of Carbon Tetrachloride

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Research Triangle Park, NC

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Locating And Estimating Air Emissions From Sources Of Carbon Tetrachloride

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with carbon tetrachloride. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of carbon tetrachloride and in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit carbon tetrachloride, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for carbon tetrachloride release into the air from each operation.

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Locating And Estimating Air Emissions From Sources Of Carbon Tetrachloride

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

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This report has been reviewed by the Office Of Air Quality Planning And Standards, U.S. Environmental Protection Agency, and has been approved for publication as received from GCA Technology. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

CONTENTS

Figures iv
Tables vi

1. Purpose of Document 1
2. Overview of Document Contents 3
3. Background. 5
    Nature of Pollutant. 5
    Overview of Production and Use 8
4. Carbon Tetrachloride Emission Sources 11
    Carbon Tetrachloride Production. 11
    Fluorocarbon Production. 26
    Carbon Tetrabromide Production 32
    Liquid Pesticide Formulation 35
    Pharmaceutical Manufacturing 39
    Use of Pesticides Containing Carbon Tetrachloride. . . . 42
    Ethylene Dichloride Production 56
    Perchloroethylene and Trichloroethylene Production 65
    Other Potential Sources of Carbon Tetrachloride Emissions. . . . 73
5. Source Test Procedures. 80

References 82
Appendix - Emission Factors for Carbon Tetrachloride Production. . . A-1
References for Appendix. A-32

FIGURES

Number Page

1 Chemical use tree for carbon tetrachloride. 10

2 Basic operations that may be used in carbon tetrachloride production by the hydrocarbon chlorinolysis process 13

3 Basic operations that may be used in carbon tetrachloride production by the methane chlorination process 15

4 Basic operations that may be used in carbon tetrachloride production by the carbon disulfide chlorination process 17

5 Basic operations that may be used in the methanol hydrochlorination/methyl chloride chlorination process 19

6 Basic operations that may be used in the production of fluorocarbons 11 and 12 27

7 Basic operations that may be used in carbon tetrabromide production 33

8 Basic operations that may be used in synthetic pharmaceutical manufacturing. 40

9 Residual carbon tetrachloride fumigant as a function of the number of days grain is aired. 51

10 Basic operations that may be used in ethylene dichloride production by the balanced process, with air-based oxychlorination 57

11 Basic operations that may be used in ethylene dichloride production by the balanced process, oxygen-based oxychlorination step. 59

12 Basic operations that may be used in perchloroethylene and trichloroethylene production by chlorination of ethylene dichloride 66

13 Basic operations that may be used in perchloroethylene and trichloroethylene production by oxychlorination of ethylene dichloride 68

Figures (continued)

Number | Page

14 Method 23 sampling train 81

A-1 Process flow diagram for hypothetical plant using hydrocarbon chlorinolysis (perchloroethylene coproduct) process A-22

A-2 Process flow diagram for hypothetical plant using methane chlorination process A-26

A-3 Process flow diagram for hypothetical plant using methanol hydrochlorination/methyl chloride chlorination process A-29

TABLES

Number Page

1 Physical Properties of Carbon Tetrachloride, CCl_4. 6

2 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Carbon Tetrachloride Production Facility (Hydrocarbon Chlorinolysis Process). 21

3 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Carbon Tetrachloride Production Facility (Methane Chlorination Process) 22

4 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Carbon Tetrachloride Production Facility (Carbon Disulfide Chlorination Process) 23

5 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Facility Using the Methanol Hydrochlorination/Methyl Chloride Chlorination Process . 24

6 Carbon Tetrachloride Production Facilities 25

7 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Facility Producing Fluorocarbons 11 and 12. 29

8 Facilities Producing Fluorocarbons 11 and 12 31

9 Carbon Tetrabromide Production Facilities. 34

10 Registrants and Applicants for Registration of Pesticidal Products Containing Carbon Tetrachloride 36

11 Carbon Tetrachloride Fumigant Brand Names. 43

12 Fumigant Application Rates 50

13 On-Farm Grain Storage. 53

14 Off-Farm Grain Storage 55

15 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors for a Hypothetical Facility Producing Ethylene Dichloride by the Balanced Process 61

16 Ethylene Dichloride Production Facilities. 64

Tables (continued)

Number Page

17 Controlled and Uncontrolled Carbon Tetrachloride Emission Factors Reported by a Plant Producing Perchloroethylene by Ethylene Dichloride Chlorination. 70

18 Facilities Producing Perchloroethylene and/or Trichloroethylene 72

19 Chlorine Production Facilities. 74

20 Phosgene Production Facilities. 78

A-1 Summary of Calculations of Carbon Tetrachloride Emission Factors A-6

A-2 Storage Tank Parameters for Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct) Process A-7

A-3 Summary of Composition Calculations for Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct) - Crude Product Storage Tank. A-9

A-4 Storage Tank Parameters for Methane Chlorination Process. A-11

A-5 Summary of Composition Calculations for Methane Chlorination - Crude Product Tank A-12

A-6 Storage Tank Parameters for Methanol Hydrochlorination/Methyl Chloride Chlorination Process. A-13

A-7 Summary of Composition Calculations for Methanol Hydrochlorination/Methyl Chloride Chlorination-Crude Product Tank. A-14

A-8 Summary of Composition Calculations for Methanol Hydrochlorination/Methyl Chloride Chlorination-Surge Tank. A-15

A-9 Storage Tank Parameters for Carbon Disulfide Chlorination Process. A-16

SECTION 1
PURPOSE OF DOCUMENT

EPA, States and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with carbon tetrachloride. Its intended audience includes Federal, State and local air pollution personnel and others who are interested in locating potential emitters of carbon tetrachloride and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on carbon tetrachloride emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about 1) the types of sources that may emit carbon tetrachloride, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for carbon tetrachloride to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment and operating practices. Thus, in situations where an accurate assessment of carbon tetrachloride emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State and local air pollution agencies and others who are interested in locating potential air emitters of carbon tetrachloride and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of carbon tetrachloride, its commonly occurring forms and an overview of its production and uses. A chemical use tree summarizes the quantities consumed in various end use categories in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

Section 4 of this document focuses on major industrial source categories that may discharge carbon tetrachloride air emissions. This section discusses the production of carbon tetrachloride, its use as an industrial feedstock, and processes which produce carbon tetrachloride as a byproduct. For each major industrial source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for carbon tetrachloride emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production or use of carbon tetrachloride, based primarily on trade publications.

The final section of this document summarizes available procedures for source sampling and analysis of carbon tetrachloride. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA has generally not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

The appendix located at the end of this document presents derivations of carbon tetrachloride emission factors for carbon tetrachloride production processes which are presented in Section 4. The development of these emission factors is discussed in detail for sources such as process vents, storage tank vents, liquid and solid waste streams, handling, and leaks from process valves, pumps, compressors, and pressure relief valves.

This document does not contain any discussion of health or other environmental effects of carbon tetrachloride, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

SECTION 3

BACKGROUND

NATURE OF POLLUTANT

Carbon tetrachloride, CCl_4, is a clear, colorless, nonflammable liquid at normal temperatures and pressures. Physical properties of carbon tetrachloride are presented in Table 1.

Carbon tetrachloride is miscible with most organic solvents, but is essentially insoluble in water. It is relatively volatile, with a vapor pressure of 11.94 kPa at 20°C.[1] Due to its high thermal capacity, carbon tetrachloride increases the lower explosion limits of gaseous mixtures and has an extinctive effect on flames. The density of carbon tetrachloride vapor is over five times that of air; thus, in cases where concentrated gaseous emissions occur, the plume will tend to settle to the ground before dispersing into the ambient air.[2]

Carbon tetrachloride decomposes in fires to phosgene. Thermal decomposition of carbon tetrachloride occurs very slowly at temperatures up to 400°C. At temperatures of 900 to 1300°C, extensive dissociation occurs forming perchloroethylene, hexachloroethane, and some chlorine. Reaction of carbon tetrachloride with steam at high temperatures results in the formation of chloromethanes, hexachloroethane, and perchloroethylene.[1]

Carbon tetrachloride is very stable in the atmosphere, with a residence time of about 30 years. Residence time is defined as the time required for the concentration to decay to 1/e of its original value (e = 2.7183).[3] The major mechanisms that remove carbon tetrachloride from the air are ultraviolet photolysis and reaction with oxygen radicals in the stratosphere.[4] The major products of carbon tetrachloride photo-oxidation are phosgene and chloride radical.[2,3]

TABLE 1. PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE, CCl_4[1]

Property	Value
Synonyms: Tetrachloromethane, methane tetrachloride, perchloromethane, benzinoform	
CAS Registry No.	56-23-5
Molecular weight	153.82
Melting point, °C	-22.92
Boiling point, °C	76.72
Refractive index, 15°C	1.46305
Specific gravity	
20/4°C	1.59472
Autoignition temperature, °C	>1,000
Flash point, °C	None
Vapor density, air = 1	5.32
Surface tension, mN/m(=dyn/cm)	
0°C	29.38
20°C	26.77
60°C	18.16
Specific heat, J/kg	
20°C	866
30°C	837
Critical temperature, °C	283.2
Critical pressure, MPa	4.6
Critical density, kg/m	558
Thermal conductivity, mW/(m·K)	
Liquid, 20°C	118
Vapor, bp	7.29
Average coefficient of volume expansion, 0-40°C	0.00124
Dielectric constant	
Liquid, 20°C	2.205
Liquid, 50°C	1.874
Vapor, 87.6°C	1.00302

CONTINUED

TABLE 1. (continued)

Property	Value
Heat of formation, kJ/mol	
Liquid	-142
Vapor	-108
Heat of combustion, liquid, at constant volume, 18.7°C, kJ/mol	365
Latent heat of fusion, kJ/mol	2.535
Latent heat of vaporization, kJ/kg	194.7
Viscosity, 20°C, mPa·s	0.965
Vapor pressure, kPa	
0°C	4.410
20°C	11.94
40°C	28.12
60°C	58.53
150°C	607.3
200°C	1,458
Solubility of CCl_4 in water, 25°C, g/100 g H_2O	0.08
Solubility of water in CCl_4, 25°C, g/100 g CCl_4	0.013

OVERVIEW OF PRODUCTION AND USE

Carbon tetrachloride was first manufactured on a large scale in the United States in 1907, primarily as a drycleaning agent and for use in fire extinguishers.[1]

Carbon tetrachloride is currently produced in the United States by five companies at nine manufacturing sites. Domestic production in 1980 was 710 million pounds. Approximately 95 million pounds of carbon tetrachloride were exported and 7 million pounds imported.[5]

Carbon tetrachloride is produced domestically by three processes: chlorinolysis of hydrocarbons, methane chlorination, and carbon disulfide chlorination. Hydrocarbon chlorinolysis (perchloroethylene coproduct), the predominant manufacturing process, involves the chlorination of hydrocarbons at high temperatures to yield carbon tetrachloride and perchloroethylene, which are then separated by distillation. The relative amounts of these two coproducts depend on the nature of the hydrocarbon starting material and conditions of chlorination.[1]

In the methane chlorination process, methane is chlorinated at a temperature of about 400°C and a pressure of about 200 kPa to produce carbon tetrachloride, methyl chloride, methylene chloride and chloroform. The chloromethane coproducts are separated by four sequential distillations. The methyl chloride in the overheads from the first column can be recycled to the chlorination reactor to enhance the yield of the other chloromethanes.[6]

In the carbon disulfide chlorination process, a solution of carbon disulfide and sulfur chloride in carbon tetrachloride is fed to a chlorination reactor where chlorine is sparged through the solution to yield a mixture of product carbon tetrachloride and sulfur chloride. The sulfur chloride is then reacted with carbon disulfide, producing carbon tetrachloride and elemental sulfur. The carbon tetrachloride produced in this reaction and excess carbon disulfide are recycled to the chlorination reactor.[7]

Carbon tetrachloride may also be produced as a byproduct of the manufacture of methyl chloride, methylene chloride, and chloroform by the methanol hydrochlorination/methyl chloride chlorination process. However, the crude carbon tetrachloride-containing bottoms from this process commonly are used on-site in the chlorinolysis process for manufacturing carbon tetrachloride and perchloroethylene.[8]

The current uses of carbon tetrachloride are listed in Figure 1 with the percentage of carbon tetrachloride consumed for each use. The major end use of carbon tetrachloride is in the production of trichlorofluoromethane (fluorocarbon 11) and dichlorodifluoromethane (fluorocarbon 12), which accounted for 81 percent of 1981 consumption. Prior to the restriction by the Environmental Protection Agency on the use of fluorocarbons as aerosol propellants, both fluorocarbons 11 and 12 were widely used for this purpose. Currently, fluorocarbon 12 is used as a refrigerant and fluorocarbon 11 is used as a blowing agent in the manufacture of plastic foams.[5]

Miscellaneous and solvent applications of carbon tetrachloride accounted for 7 percent of 1981 consumption. These applications include use as a feedstock in carbon tetrabromide manufacture;[2] in pesticide formulations; as a solvent in pharmaceutical manufacture; and as a solvent and thinner in shoe and furniture polishes, paints, lacquers, printing inks, floor waxes, and stains.[5] The use of carbon tetrachloride in fire extinguishers has been discontinued because of its tendency to decompose and form phosgene when sprayed into flames.[7]

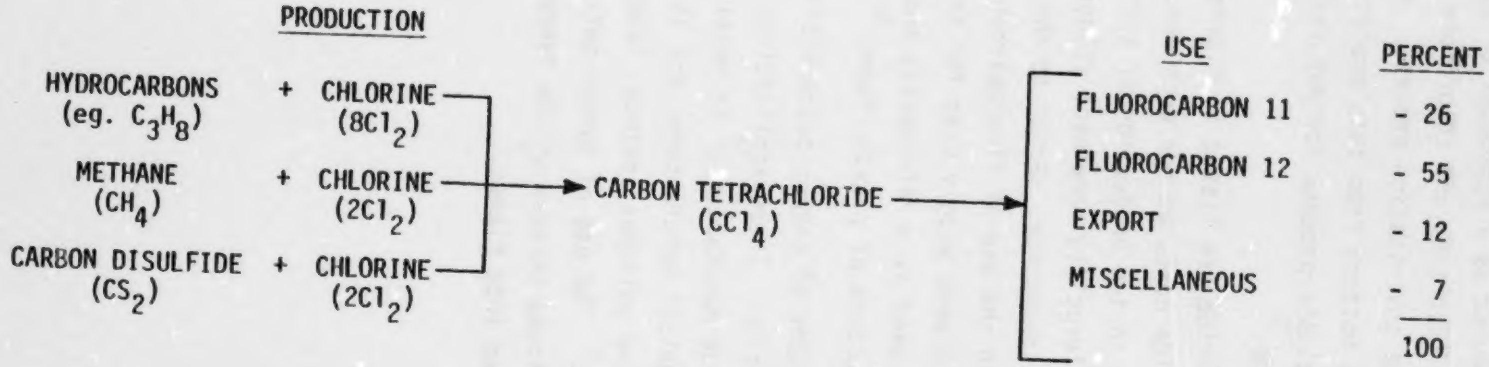

PRODUCTION
HYDROCARBONS (eg. C_3H_8)
+
CHLORINE ($8Cl_2$)
METHANE (CH_4)
+
CHLORINE ($2Cl_2$)
CARBON DISULFIDE (CS_2)
+
CHLORINE ($2Cl_2$)
CARBON TETRACHLORIDE (CCl_4)
USE
FLUOROCARBON 11
FLUOROCARBON 12
EXPORT
MISCELLANEOUS
PERCENT
- 26
- 55
- 12
- 7
100

Figure 1. Chemical use tree for carbon tetrachloride.[5]

SECTION 4

CARBON TETRACHLORIDE EMISSION SOURCES

This section discusses carbon tetrachloride emissions from direct sources such as carbon tetrachloride production, fluorocarbon production, carbon tetrabromide production, liquid pesticide formulation, pharmaceutical manufacture, and the use of pesticides containing carbon tetrachloride. Indirect emission sources are also discussed. Indirect sources of carbon tetrachloride include ethylene dichloride production and the manufacture of perchloroethylene and trichloroethylene. Process and emissions information are presented for each source for which data are available.

CARBON TETRACHLORIDE PRODUCTION

In the most widely used carbon tetrachloride production process, the chlorinolysis process, hydrocarbons are chlorinated at or near pyrolytic conditions to produce a mixture of carbon tetrachloride and perchloroethylene. A second process involves the direct chlorination of methane to produce chloromethanes, including carbon tetrachloride. Direct chlorination of methane is used currently at only one plant.[10] Another facility formerly employed this process but has changed to a different production process. The details of this new process are not currently available.[11] Carbon tetrachloride is also produced by the chlorination of carbon disulfide at one facility. In addition, carbon tetrachloride is formed as a byproduct in the manufacture of chloroform and methylene chloride by the hydrochlorination of methyl chloride in the methanol hydrochlorination/methyl chloride chlorination process. This process is included in this section because it is integrated at many facilities with the chlorinolysis process. At these facilities, the impure carbon tetrachloride from methyl chloride chlorination is frequently used as feedstock for the chlorinolysis process.[12]

Process Descriptions

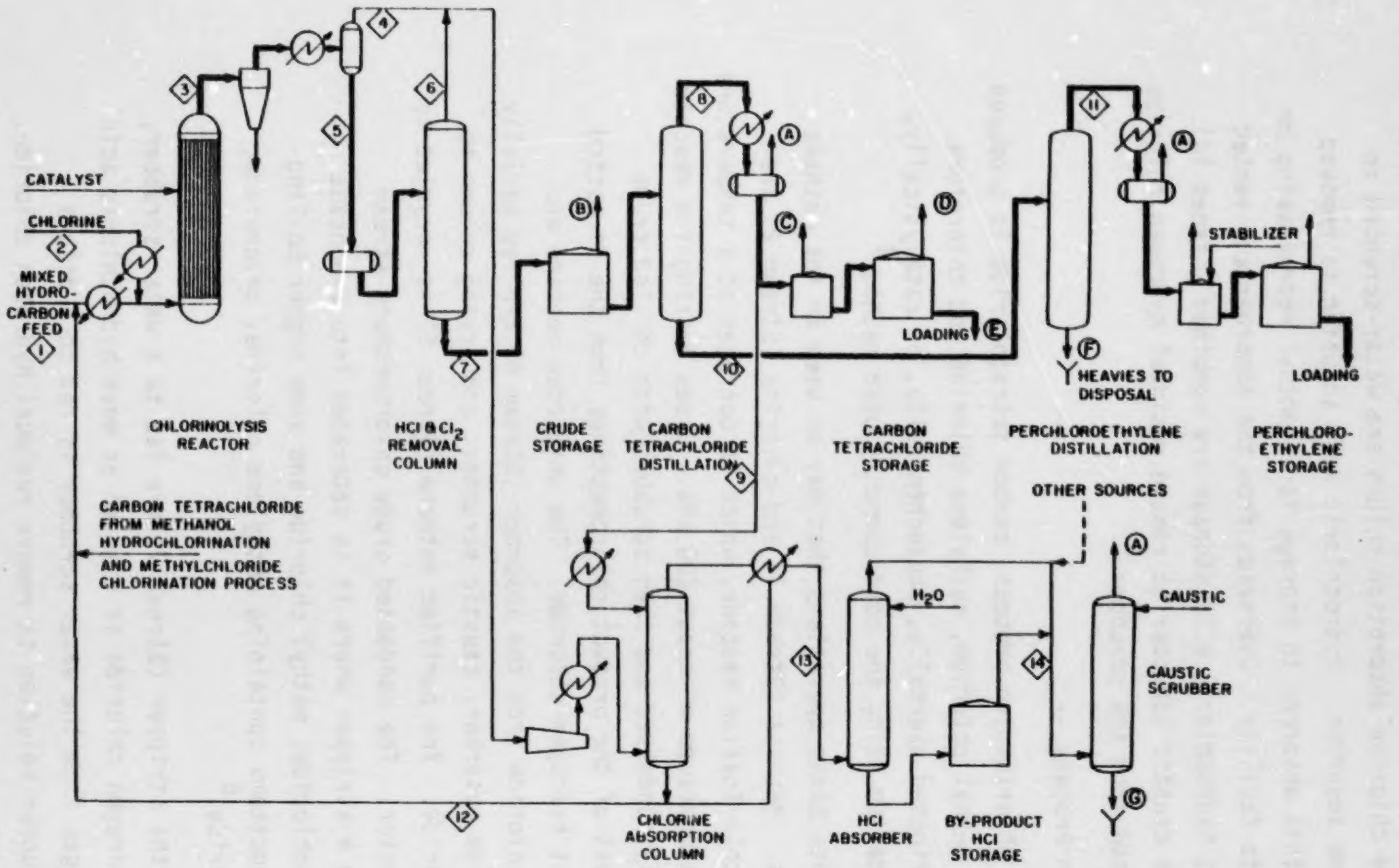
Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct) Process --

The major products of the chlorinolysis process are carbon tetrachloride and perchloroethylene. A variety of hydrocarbons and chlorinated hydrocarbons may be used as feed materials including crude carbon tetrachloride, ethylene dichloride, acetylene, ethylene, propylene, paraffinic hydrocarbons of up to four carbons, and napthalene.[1,8]

Basic operations that may be used in the chlorinolysis process are shown in Figure 2. Preheated feed material (Stream 1) and chlorine (Stream 2) are fed to the chlorinolysis reactor, a fluid bed reactor maintained at about 500°C which contains copper and barium chloride on graphite as a catalyst.[8]

The reaction products (Stream 3) pass through a cyclone for removal of entrained catalyst and then on to a condenser. Uncondensed materials (Stream 4), consisting of hydrogen chloride, unreacted chlorine, and some carbon tetrachloride, are removed to the hydrogen chloride purification system. The condensed reactor products (Stream 5) are fed to a hydrogen chloride and chlorine removal column, with the overheads (Stream 6) from this column going to the hydrogen chloride purification operation. The bottoms (Stream 7) from the column are fed to a crude storage tank. Material from crude storage is fed to a series of two distillation columns. The first column extracts carbon tetrachloride (Stream 8) which is transferred either to a storage and loading operation or to the hydrogen chloride purification system (Stream 9) for use as a scrubber liquid. The bottoms (Stream 10) from the carbon tetrachloride distillation column are fed to a perchloroethylene distillation column. In this column, perchloroethylene is extracted as overheads (Stream 11) and transferred to storage and loading. Bottoms from the perchloroethylene distillation column are incinerated.[8]

The feed streams (Streams 4 and 6) to the hydrogen chloride purification operation are compressed, cooled, and scrubbed in a chlorine absorption column with chilled carbon tetrachloride (Stream 9) to remove chlorine. The bottoms and condensable overheads (Stream 12) from this column are


CATALYST
CHLORINE
MIXED HYDRO-CARBON FEED
1
2
3
4
5
6
7
8
9
10
11
12
13
14
A
B
C
D
E
F
G
CHLORINOLYSIS REACTOR
HCl & Cl_2 REMOVAL COLUMN
CRUDE STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE STORAGE
LOADING
HEAVIES TO DISPOSAL
PERCHLOROETHYLENE DISTILLATION
STABILIZER
PERCHLORO-ETHYLENE STORAGE
LOADING
CARBON TETRACHLORIDE FROM METHANOL HYDROCHLORINATION AND METHYLCHLORIDE CHLORINATION PROCESS
CHLORINE ABSORPTION COLUMN
H_2O
HCl ABSORBER
BY-PRODUCT HCl STORAGE
OTHER SOURCES
CAUSTIC
CAUSTIC SCRUBBER

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 2. Basic operations that may be used for carbon tetrachloride production by the hydrocarbon chlorinolysis (perchloroethylene coproduct) process.[8]

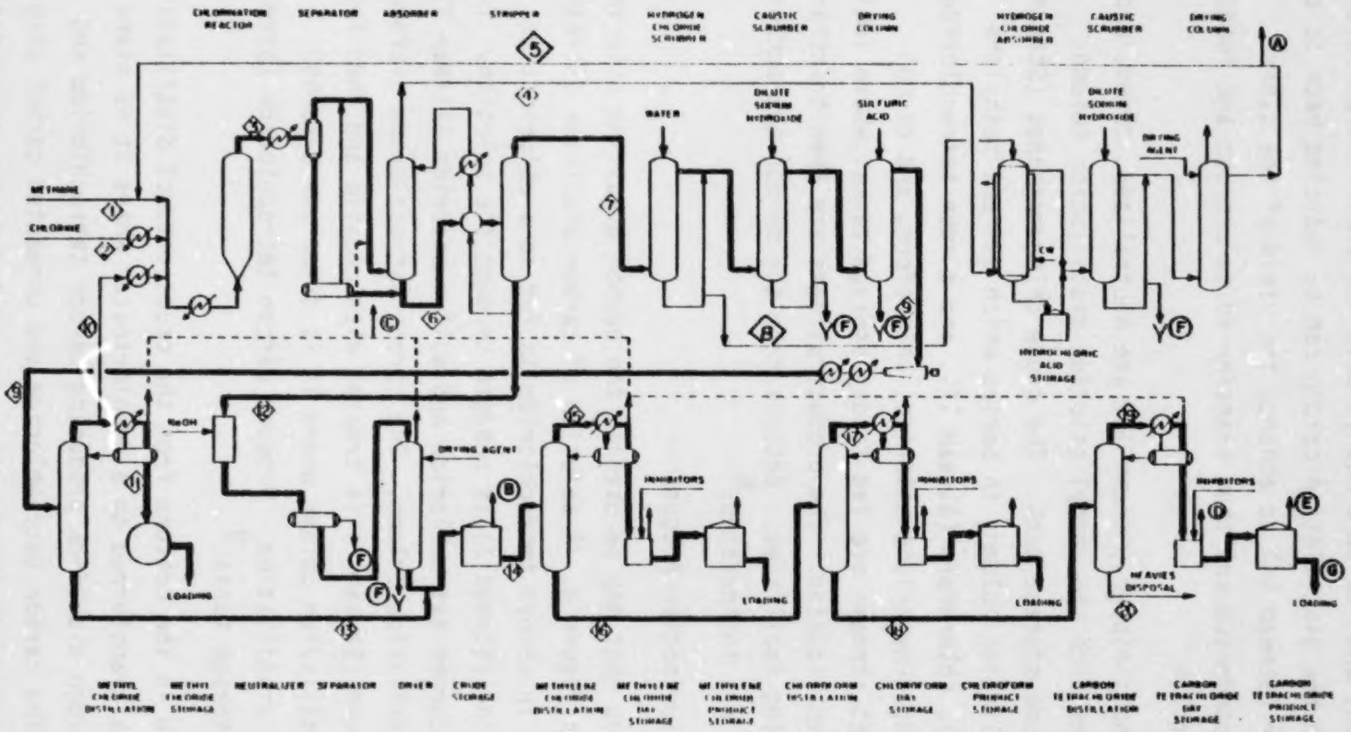
combined and recycled to the chlorinolysis reactor. Uncondensed overheads (Stream 13) from the chlorine absorption column are water-scrubbed in the hydrogen chloride absorber. Hydrochloric acid solution is removed from the bottom of this absorber to storage for eventual reprocessing or for use in a separate facility. Overheads from the absorber and vented gases from byproduct hydrochloric acid storage are combined (Stream 14) and passed through a caustic scrubber to remove residual hydrogen chloride. Inert gases are vented from the scrubber.[8]

Methane Chlorination Process --

In the methane chlorination process, carbon tetrachloride is produced as a coproduct with methyl chloride, methylene chloride and chloroform. Methane can be chlorinated thermally, photochemically, or catalytically, with thermal chlorination being the most commonly used method.[6]

Figure 3 presents basic operations that may be used in the methane chlorination process. Methane (Stream 1) and chlorine (Stream 2) are mixed and fed to a chlorination reactor, which is operated at a temperature of about 400°C and a pressure of about 200 kPa. Gases exiting the reactor (Stream 3) are partly condensed and then scrubbed with chilled crude product to absorb most of the product chloromethanes from the unreacted methane and byproduct hydrogen chloride. The unreacted methane and byproduct hydrogen chloride from the absorber (Stream 4) are fed serially to a hydrogen chloride absorber, caustic scrubber, and drying column to remove hydrogen chloride. The purified methane (Stream 5) is recycled to the chlorination reactor. The condensed crude chloromethane stream (Stream 6) is fed to a stripper where it is separated into overheads containing hydrogen chloride; methyl chloride and some higher boiling chloromethanes; and bottoms containing methylene chloride, chloroform, and carbon tetrachloride.[6]

Overheads from the stripper (Stream 7) are fed to a water scrubber, where most of the hydrogen chloride is removed as weak hydrochloric acid (Stream 8). The offgas from the water scrubber is fed to a dilute sodium hydroxide scrubber solution to remove residual hydrogen chloride. Water is then removed from the crude chloromethanes in a drying column.


CHLORINATION REACTOR
SEPARATOR
ABSORBER
STRIPPER
HYDROGEN CHLORIDE SCRUBBER
CAUSTIC SCRUBBER
DRYING COLUMN
HYDROGEN CHLORIDE ABSORBER
CAUSTIC SCRUBBER
DRYING COLUMN
METHANE
CHLORINE
WATER
DILUTE SODIUM HYDROXIDE
SULFURIC ACID
DILUTE SODIUM HYDROXIDE
DRYING AGENT
CW
HYDROCHLORIC ACID STORAGE
NaOH
DRYING AGENT
INHIBITORS
INHIBITORS
INHIBITORS
LOADING
LOADING
LOADING
HEAVIES DISPOSAL
LOADING
A
B
C
D
E
F
G
METHYL CHLORIDE DISTILLATION
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NEUTRALIZER
SEPARATOR
DRYER
CRUDE STORAGE
METHYLENE CHLORIDE DISTILLATION
METHYLENE CHLORIDE DAY STORAGE
METHYLENE CHLORIDE PRODUCT STORAGE
CHLOROFORM DISTILLATION
CHLOROFORM DAY STORAGE
CHLOROFORM PRODUCT STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE DAY STORAGE
CARBON TETRACHLORIDE PRODUCT STORAGE

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 3. Basic operations that may be used for carbon tetrachloride production by the methane chlorination process.[6]

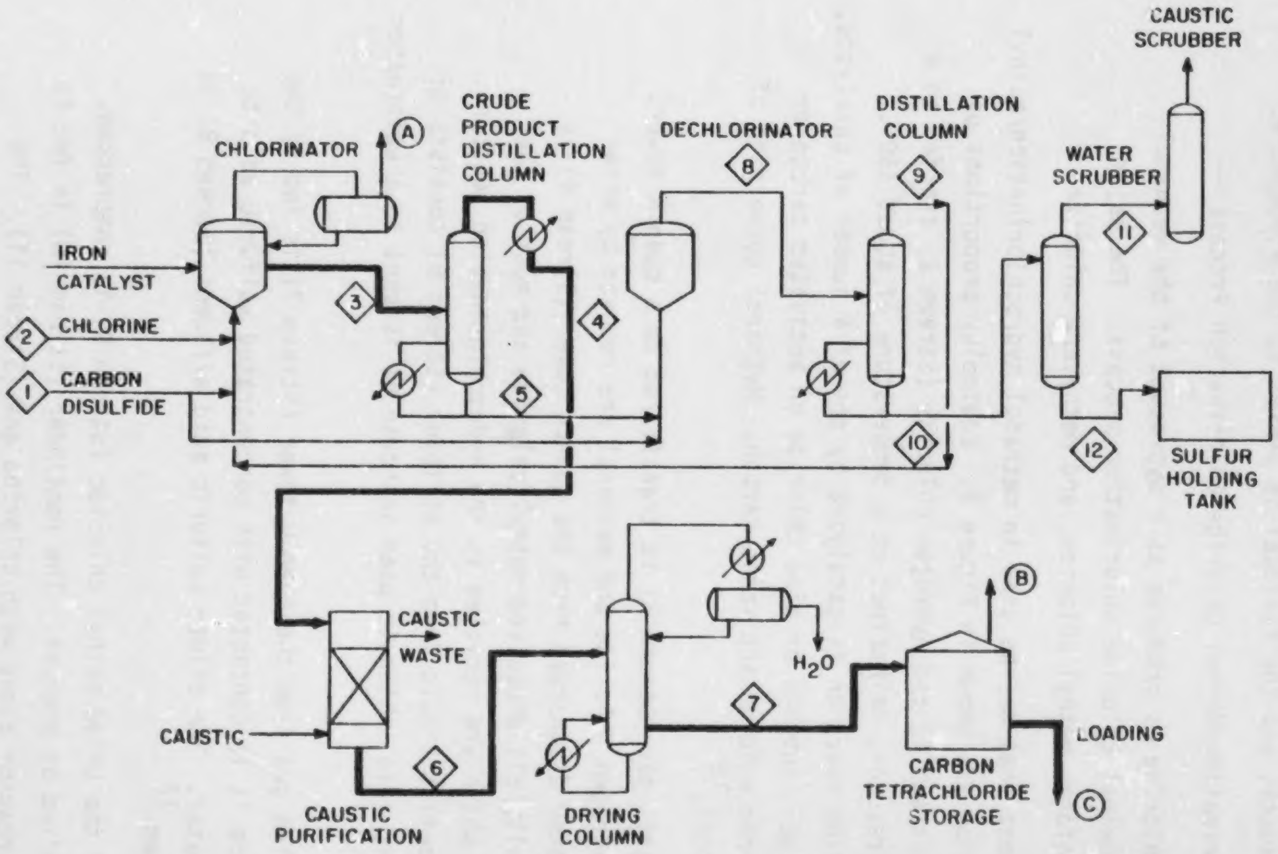
The chloromethane mixture from the drying column (Stream 9) is compressed, condensed, and fed to a methyl chloride distillation column. Methyl chloride from the distillation column can be recycled back to the chlorination reactor (Stream 10) to enhance the yield of the other chloromethanes, or condensed and then transferred to storage and loading as a product (Stream 11).[6]

Bottoms from the stripper (Stream 12) are neutralized, dried, and combined with bottoms from the methyl chloride distillation column (Stream 13) in a crude storage tank. The crude chloromethanes (Stream 14) pass to three distillation columns in series which extract methylene chloride (Stream 15), chloroform (Stream 17), and carbon tetrachloride (Stream 19). Condensed methylene chloride, chloroform, and carbon tetrachloride product streams are fed to day storage tanks, where inhibitors may be added for stabilization. The product streams are then transferred to storage and loading facilities. Bottoms from the carbon tetrachloride distillation column are incinerated.[6]

Carbon Disulfide Chlorination Process --

Basic operations that may be used in the carbon disulfide chlorination process are shown in Figure 4. A solution of carbon disulfide (Stream 1) and sulfur chloride in carbon tetrachloride is fed to a chlorination reactor where chlorine (Stream 2) is sparged through the solution. The reaction products, carbon tetrachloride and sulfur chloride (Stream 3), are pumped to a distillation column. The carbon tetrachloride overhead stream from the column (Stream 4) is treated with caustic and then fed (Stream 6) to a distillation column where it is dried via a carbon tetrachloride-water distillation. Product carbon tetrachloride (Stream 7) is then pumped to storage tanks.[9]

Sulfur chloride in the bottoms from the crude product distillation column (Stream 5) is transferred to a dechlorinator where it is mixed and reacted with carbon disulfide producing carbon tetrachloride and elemental sulfur. The carbon tetrachloride and unreacted carbon disulfide (Stream 8) are distilled off (Stream 9) and recycled to the chlorination reactor. Residual sulfur and sulfur chloride (Stream 10) are pumped to


CAUSTIC SCRUBBER
CRUDE PRODUCT DISTILLATION COLUMN
DISTILLATION COLUMN
CHLORINATOR
A
DECHLORINATOR
8
9
WATER SCRUBBER
IRON CATALYST
11
3
4
2
CHLORINE
1
CARBON DISULFIDE
5
10
12
SULFUR HOLDING TANK
B
CAUSTIC WASTE
H_2O
7
CAUSTIC
LOADING
6
CARBON TETRACHLORIDE STORAGE
C
CAUSTIC PURIFICATION
DRYING COLUMN

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 4. Basic operations that may be used for carbon tetrachloride production by the carbon disulfide chlorination process.[7,9]

a water scrubber where the sulfur chloride is removed from the sulfur. The sulfur byproduct (Stream 12) is transferred to a holding tank and from there as needed to a sulfuric acid plant. Sulfur chloride (Stream 11) is scrubbed with caustic and the residual is vented to the atmosphere.[9]

Methanol Hydrochlorination/Methyl Chloride Chlorination Process --

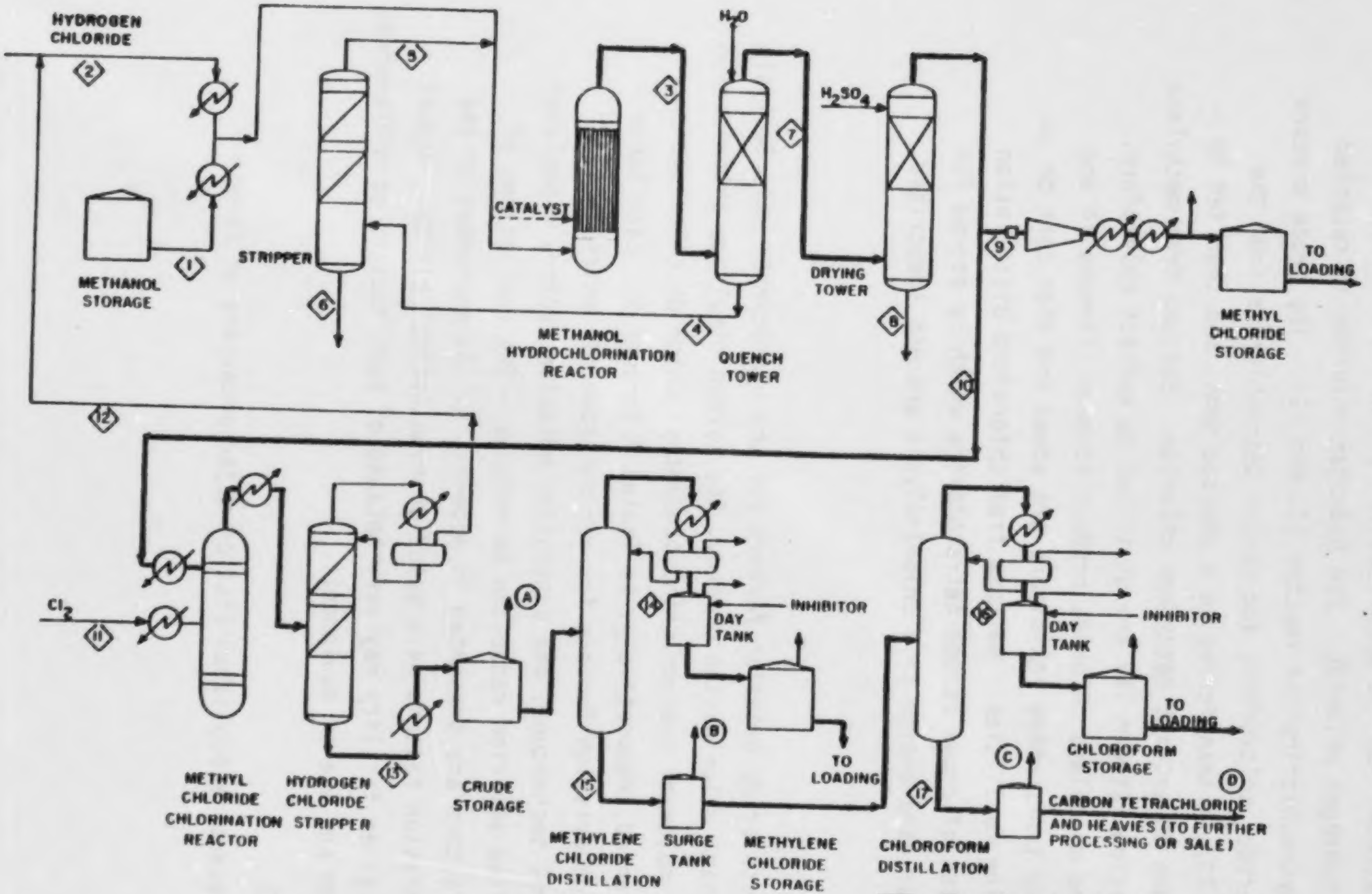
Carbon tetrachloride is produced as a byproduct of the methanol hydrochlorination/methyl chloride chlorination process. The major products are chloroform, methyl chloride, and methylene chloride.

Basic operations that may be used in methanol hydrochlorination/methyl chloride chlorination are shown in Figure 5. Equimolar proportions of gaseous methanol (Stream 1) and hydrogen chloride (Stream 2) are fed to a hydrochlorination reactor, maintained at a temperature of about 350°C. The hydrochlorination reaction is catalyzed by one of a number of catalysts, including alumina gel, cuprous or zinc chloride on activated carbon or pumice, or phosphoric acid on activated carbon. Methanol conversion of 95 percent is typical.[12]

The reactor exit gas (Stream 3) is transferred to a quench tower, where unreacted hydrogen chloride and methanol are removed by water scrubbing. The water discharged from the quench tower (Stream 4) is stripped of virtually all dissolved methyl chloride and most of the methanol, both of which are recycled to the hydrochlorination reactor (Stream 5). The outlet liquid from the stripper (Stream 6) consists of dilute hydrochloric acid, which is used in-house or is sent to a wastewater treatment system.[12]

Methyl chloride gas from the quench tower (Stream 7) is fed to the drying tower, where it is contacted with concentrated sulfuric acid to remove residual water. The dilute sulfuric acid effluent (Stream 8) is sold or reprocessed.[12]

A portion of the dried methyl chloride (Stream 9) is compressed, cooled, and liquefied as product. The remainder (Stream 10) is fed to the chlorination reactor along with chlorine gas (Stream 11). The methyl chloride and chlorine react to form methylene chloride and chloroform, along with hydrogen chloride and a small amount of carbon tetrachloride.[12]


HYDROGEN CHLORIDE
2
METHANOL STORAGE
1
STRIPPER
5
6
CATALYST
METHANOL HYDROCHLORINATION REACTOR
3
4
H_2O
QUENCH TOWER
7
H_2SO_4
DRYING TOWER
8
9
10
TO LOADING
METHYL CHLORIDE STORAGE
12
Cl_2
11
METHYL CHLORIDE CHLORINATION REACTOR
HYDROGEN CHLORIDE STRIPPER
13
A
CRUDE STORAGE
14
INHIBITOR
DAY TANK
15
B
SURGE TANK
METHYLENE CHLORIDE DISTILLATION
TO LOADING
METHYLENE CHLORIDE STORAGE
16
INHIBITOR
DAY TANK
TO LOADING
CHLOROFORM STORAGE
17
C
D
CARBON TETRACHLORIDE AND HEAVIES (TO FURTHER PROCESSING OR SALE)
CHLOROFORM DISTILLATION

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 5. Basic operations that may be used in the methanol hydrochlorination/ methyl chloride chlorination process.[12]

The product stream from the chlorination reactor is condensed and then stripped of hydrogen chloride. The hydrogen chloride is recycled to the methanol hydrochlorination reactor (Stream 12). The crude mixture of methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 13) is transferred to a storage tank, and then fed to a distillation column to extract methylene chloride. Bottoms from methylene chloride distillation (Stream 15) are distilled to extract chloroform. The chloroform and methylene chloride product streams (Streams 14 and 16) are fed to day tanks where inhibitors are added and then sent on to storage and loading facilities. Bottoms from chloroform distillation (Stream 17) consist of crude carbon tetrachloride which is stored for subsequent sale or used onsite in a chlorinolysis process (described previously).[12]

Emissions

Carbon tetrachloride emission factors for the hydrocarbon chlorinolysis process, the methane chlorination process, the carbon disulfide chlorination process, and the methanol hydrochlorination/methyl chloride chlorination process are presented, respectively, in Tables 2 through 5. Each table lists uncontrolled emission factors for various sources, potentially applicable control techniques, and controlled emission factors associated with the identified emission reduction techniques. The derivations of these emission factors are presented in Appendix A. As described in the appendix, the emission factors were based on hypothetical plants. Actual emissions for a given facility may vary because of such factors as differences in process design and age of equipment.

Source Locations

Table 6 presents a published list of major producers of carbon tetrachloride.

TABLE 2. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL CARBON TETRACHLORIDE PRODUCTION FACILITY (HYDROCARBON CHLORINOLYSIS PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor[c]	Potentially applicable control technique[d]	% reduction	Controlled carbon tetrachloride emission factor[c]
Distillation column	A	0.008 kg/Mg	None	--	--
Storage					
Crude tank	B	0.098 kg/Mg	Refrigerated condenser	87	0.013 kg/Mg
Day tanks (2)	C	0.45 kg/Mg	Refrigerated condenser	93	0.032 kg/Mg
Carbon tetrachloride tank	D	0.58 kg/Mg	Refrigerated condenser	85	0.087 kg/Mg
Handling[e]	E	0.24 kg/Mg	Refrigerated condenser	85	0.036 kg/Mg
Secondary					
Hex waste handling and disposal and waste hydrocarbon storage	F	0.0046 kg/Mg	Vapor balance and refrigerated condenser	99	4.6×10^{-5} kg/Mg
Waste caustic	G	0.0029 kg/Mg	Steam stripper	96	1.2×10^{-4} kg/Mg
Process fugitive[f]		1.5 kg/hr	Quarterly I/M of pumps and and valves[g]	48	0.78 kg/hr
			Monthly I/M of pumps and and valves	64	0.54 kg/hr
			Monthly I/M of valves; double mechanical seals on pumps; rupture disks on relief valves	73	0.41 kg/hr

---

[a] Any given carbon tetrachloride production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 2.

[c] Emission factors in terms of kg/Mg refer to kilogram of carbon tetrachloride emitted per megagram of carbon tetrachloride produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -15°C and uncontrolled emission temperatures of 20°C for product storage and handling, of 38°C for crude storage, and of 35°C for day storage tanks. Greater removal efficiency can be achieved by using lower operating temperatures. For secondary emissions, potentially applicable control techniques and associated emission reductions are from reference 8. For fugitive emissions, the derivations of the emission reductions associated with the control alternatives from reference 13 are given in Appendix A.

[e] Loading of trucks, tank cars, barges.

[f] Fugitive emission rate is independent of plant capacity.

[g] I/M refers to inspection and maintenance.

TABLE 3. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL CARBON TETRACHLORIDE PRODUCTION FACILITY (METHANE CHLORINATION PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor[c]	Potentially applicable control technique	% reduction[d]	Controlled carbon tetrachloride emission factor[c]
Recycled methane inert gas purge vent	A	<0.042 kg/mg	None	--	--
Distillation area emergency inert gas vent	C	0.052 kg/Mg	None	--	--
Storage					
Crude tank	B	0.057 kg/Mg	Refrigerated condenser	92	0.0046 kg/Mg
Day tanks (2)	D	0.36 kg/Mg	Refrigerated condenser	93	0.025 kg/Mg
Product tank	E	0.64 kg/Mg	Refrigerated condenser	85	0.096 kg/Mg
Secondary	F	0.018 kg/Mg	None	--	--
Handling[e]	G	0.24 kg/Mg	Refrigerated condenser	85	0.036 kg/Mg
Process fugitive[f]		2.56 kg/hr	Quarterly I/M of pumps and valves[g]	49	1.6 kg/hr
			Monthly I/M of pumps and valves	64	1.1 kg/hr
			Monthly I/M of valves; double mechanical seals on pumps; rupture disks on relief valves	75	0.74 kg/hr

[a] Any given carbon tetrachloride production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 3.

[c] Emission factors in terms of kg/Mg refer to kilogram of carbon tetrachloride emitted per megagram of carbon tetrachloride produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -15°C and uncontrolled emission temperatures from reference 6 of 20°C for product storage and handling and of 35°C for the crude and day storage tanks. Greater removal efficiency can be achieved by using a lower operating temperature. For fugitive emissions, the derivations of the emission reductions associated with the control alternatives from reference 13 are given in Appendix A.

[e] Loading of trucks, tank cars, barges.

[f] Fugitive emission rate is independent of plant capacity.

[g] I/M refers to inspection and maintenance.

TABLE 4. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL CARBON TETRACHLORIDE PRODUCTION FACILITY (CARBON DISULFIDE CHLORINATION PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor[c]	Potentially applicable control technique[d]	% reduction	Controlled carbon tetrachloride emission factor[c]
Chlorinator	A	116 kg/Mg	Refrigerated condenser	95	5.8 kg/Mg
Storage	B	0.76 kg/Mg	Refrigerated condenser	85	0.11 kg/Mg
Handling[e]	C	0.24 kg/Mg	Refrigerated condenser	85	0.036 kg/Mg
Process fugitive		0.60 kg/Mg[f]	Quarterly I/M of pumps and valves[g]	46	0.32 kg/Mg
			Monthly I/M of pumps and valves	63	0.22 kg/Mg
			Monthly I/M of valves: double mechanical seals on pumps; rupture disks on relief valves	76	0.14 kg Mg

---

[a] Any given carbon tetrachloride production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated to Figure 4.

[c] Emission factors in terms of kg/mg refer to kilogram of carbon tetrachloride emitted per megagram of carbon tetrachloride produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -15°C and uncontrolled emission temperatures of 20°C for product storage and handling. Greater removal efficiency can be achieved by using lower operating temperatures. For process fugitives, control techniques were derived from Reference 13. Because information on the number of process fugitive emission sources was not available, the calculation of emission reduction achievable in this process was not possible. The emission reductions were estimated as the averages of achievable emission reductions calculated for the other carbon tetrachloride production processes.

[e] Loading of trucks, tank cars, barges.

[f] Reference 14.

[g] I/M refers to inspection and maintenance.

TABLE 5. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE PRODUCTION EMISSION FACTORS FOR A HYPOTHETICAL PLANT USING THE METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION PROCESS[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor[c]	Potentially applicable control technique	% reduction[d]	Controlled carbon tetrachloride emission factor[c]
Storage					
Crude tank	A	0.040 kg/Mg	Refrigerated condenser	97	0.0012 kg/Mg
Surge tank	B	0.057 kg/Mg	Refrigerated condenser	96	0.0023 kg/Mg
Carbon tetrachloride and heavies tank	C	1.39 kg/Mg	Refrigerated condenser	85	0.21 kg/Mg
Handling[e]	D	0.52 kg/Mg	Refrigerated condenser	85	0.078 kg/Mg
Process fugitive[f]		0.48 kg/Mg	Quarterly I/M of pumps and valves[g]	42	0.28 kg/hr
			Monthly I/M of pumps and valves	60	0.19 kg/hr
			Monthly I/M of valves; double mechanical seals on pumps; rupture disks on relief valves	81	0.091 kg/hr

[a] Any given carbon tetrachloride production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated in Figure 5.

[c] Emission factors in terms of kg/Mg refer to kilogram of carbon tetrachloride emitted per megagram of carbon tetrachloride produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -15°C and uncontrolled emission temperatures from reference 8 of 40°C for carbon tetrachloride byproduct storage and handling, of 35°C for crude storage, and of 40°C for the surge tank. Greater removal efficiency can be achieved by using lower operating temperatures. For fugitive emissions, the derivations of the emission reductions associated with the control alternatives from reference 13 are given in Appendix A.

[e] Emission factor for loading of trucks, tank cars, and barges developed for cases in which impure byproduct carbon tetrachloride is not transferred for further processing at hydrocarbon chlorinolysis cofacility.

[f] Fugitive emission rate is independent of plant capacity.

[g] I/M refers to inspection and maintenance.

TABLE 6. CARBON TETRACHLORIDE PRODUCTION FACILITIES[15]

Company	Location	Production process
Dow Chemical U.S.A.	Freeport, TX	NA
	Pittsburg, CA	Hydrocarbon chlorinolysis Methane chlorination
	Plaquemine, LA	Hydrocarbon chlorinolysis Methyl chloride chlorination
E.I. duPont de Nemours and Co.[a]	Corpus Christi, TX	Methane and ethylene chlorination with perchloroethylene coproduct
LCP Chemicals and Plastics, Inc.	Moundsville, WV	Methane chlorination Methyl chloride chlorination
Stauffer Chemical Co.	Lemoyne, AL	Carbon disulfide chlorination
	Louisville, KY	Methane chlorination Methyl chloride chlorination
Vulcan Materials Co.	Geismar, LA	Hydrocarbon chlorinolysis Methyl chloride chlorination
	Wichita, KS	Hydrocarbon chlorinolysis Methane chlorination Methyl chloride chlorination
Diamond Shamrock Corp.	Belle, WV	Methyl chloride chlorination

[a] The duPont facility is actually located in Ingleside, TX.[16] This plant produces carbon tetrachloride with perchloroethylene as a coproduct but does not use a chlorinolysis process.[17]

NA = Not available

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel.

FLUOROCARBON PRODUCTION

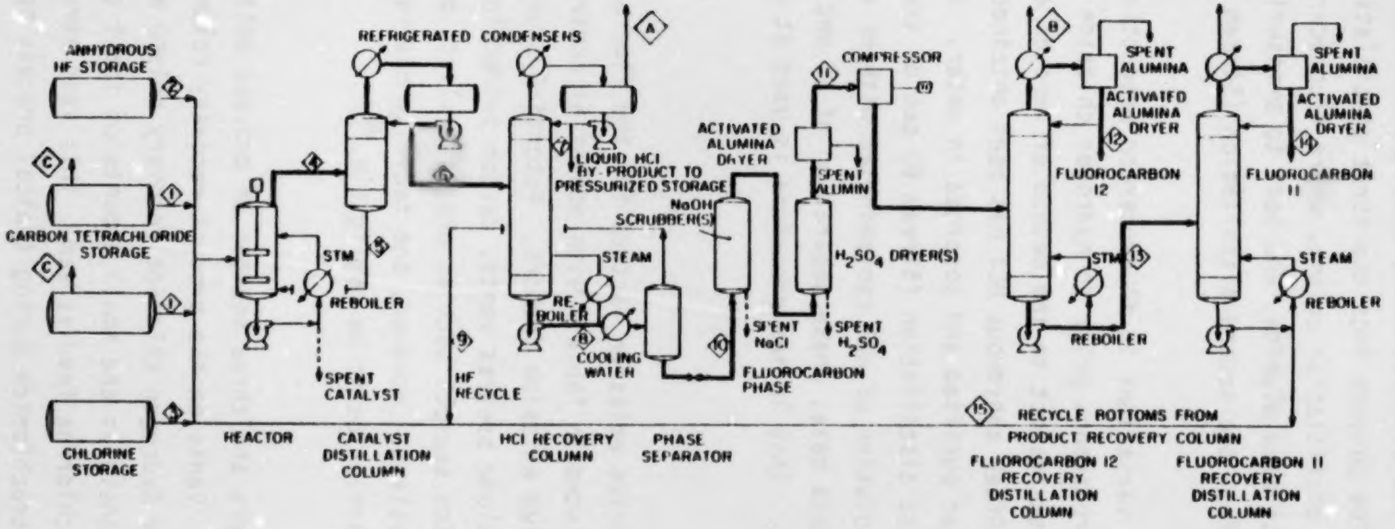
The primary use for carbon tetrachloride is as a feedstock for the production of dichlorodifluoromethane (fluorocarbon 12) and trichlorofluoromethane (fluorocarbon 11). Currently, fluorocarbon 12 is used as a refrigerant and fluorocarbon 11 is used as a blowing agent in the manufacture of plastic foams.[5]

Process Description

Fluorocarbons 11 and 12 are produced by the liquid-phase reaction of anhydrous hydrogen fluoride (HF) and carbon tetrachloride. Basic operations that may be used in the fluorocarbon production process are shown in Figure 6. Carbon tetrachloride (Stream 1), liquid anhydrous HF (Stream 2), and chlorine (Stream 3) are pumped from storage to the reactor, along with the recycled bottoms from the product recovery column (Stream 15) and the HF recycle stream (Stream 9). The reactor contains antimony pentachloride catalyst[18] and is operated at temperatures ranging from 0 to 200°C and pressures of 100 to 3,400 kPa.[19]

Vapor from the reactor (Stream 4) is fed to a catalyst distillation column, which removes as overheads hydrogen chloride (HCl), the desired fluorocarbon products, and some HF (Stream 6). Bottoms containing vaporized catalyst, unconverted and underfluorinated species, and some HF (Stream 5) are returned to the reactor. The overhead stream from the column (Stream 6) is condensed and pumped to the HCl recovery column.[18]

Anhydrous HCl byproduct is removed as overheads (Stream 7) from the HCl recovery column, condensed, and transferred to pressurized storage as a liquid. The bottoms stream from the HCl recovery column (Stream 8) is chilled until it separates into two immiscible phases: an HF phase and a denser fluorocarbon phase. These are separated in a phase separator. The HF phase (Stream 9), which contains a small amount of dissolved fluorocarbons, is recycled to the reactor. The denser phase (Stream 10), which contains the fluorocarbons plus trace amounts of HF and HCl, is evaporated and ducted to a caustic scrubber to neutralize the HF and HCl. The stream is then contacted with sulfuric acid and subsequently with activated alumina to remove water.[18]


ANHYDROUS HF STORAGE
CARBON TETRACHLORIDE STORAGE
CHLORINE STORAGE
REACTOR
CATALYST DISTILLATION COLUMN
HCl RECOVERY COLUMN
PHASE SEPARATOR
REFRIGERATED CONDENSERS
LIQUID HCl BY-PRODUCT TO PRESSURIZED STORAGE
STM
REBOILER
SPENT CATALYST
HF RECYCLE
STEAM
RE-BOILER
COOLING WATER
NaOH SCRUBBER(S)
SPENT NaCl
FLUOROCARBON PHASE
ACTIVATED ALUMINA DRYER
SPENT ALUMIN
H_2SO_4 DRYER(S)
SPENT H_2SO_4
COMPRESSOR
SPENT ALUMINA
ACTIVATED ALUMINA DRYER
FLUOROCARBON 12
FLUOROCARBON 11
STM
REBOILER
STEAM
REBOILER
RECYCLE BOTTOMS FROM PRODUCT RECOVERY COLUMN
FLUOROCARBON 12 RECOVERY DISTILLATION COLUMN
FLUOROCARBON 11 RECOVERY DISTILLATION COLUMN
A
B
C
C
1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 6. Basic operations that may be used in the production of fluorocarbons 11 and 12.[18]

The neutralized and dried fluorocarbon mixture (Stream 11) is compressed and sent to a series of two distillation columns. Fluorocarbon 12 is taken as overheads from the first column, dried with activated alumina, and sent to pressurized storage (Stream 12). The bottoms from the first distillation (Stream 13) are sent to the second distillation column, where fluorocarbon 11 is removed overhead, dried with activated alumina, and sent to pressurized storage (Stream 14). The bottoms from the second distillation (Stream 15) are recycled to the reactor.[18]

There are a number of process variations in fluorocarbon production. HF may be separated from product fluorocarbons prior to hydrogen chloride removal. The HCl removal system can vary with respect to the method of removal and the type of byproduct acid obtained. After anhydrous HCl has been obtained as shown in Figure 6, it can be further purified and absorbed in water. Alternatively, the condensed overhead from catalyst distillation (Stream 6) can be treated with water to recover an aqueous solution of HCl contaminated with HF and possibly some fluorocarbons. In this case, phase separation of HF and products, and HF recycle are not carried out. This latter procedure is used at many older plants in the industry.[18]

Emissions

Uncontrolled carbon tetrachloride emission factors for the fluorocarbon 11 and 12 production processes are listed in Table 7 with potential control techniques and associated controlled emission factors. Potential sources of carbon tetrachloride emissions include process vents, carbon tetrachloride storage tanks, and fugitive emission sources such as process valves, pumps, compressors, and pressure relief valves. However, one facility has reported fugitive emissions of carbon tetrachloride to be negligible.[20]

Process Emissions --

As indicated in Figure 6, there are three sources of process emissions in the manufacture of fluorocarbons. Vents on the product recovery columns emit only fluorocarbons. A vent on the hydrogen chloride recovery column accumulator (Vent A, Figure 6) purges noncondensibles and small amounts of inert gases which enter the reactor with the chlorine feed stream. This vent stream is not reported to contain carbon tetrachloride during typical process operation.

TABLE 7. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL FACILITY PRODUCING FLUOROCARBONS 11 and 12[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor[c]	Potentially applicable control technique	% reduction	Controlled carbon tetrachloride emission factor[c]
Reactor venting	A	0.042 kg/Mg	Vacuum jet[d]	0	0.042 kg/Mg
Distillation column	B	NA	Refrigerated condenser & carbon carbon tetrachloride scrubber[e]	NA	0.023 kg/Mg
Storage	C	0.19[f] to 0.74[g]	Refrigerated condenser[h]	85	0.029 to 0.11 kg/Mg

[a] Any given flurocarbon production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated to Figure 6.

[c] Emission factors in terms of kg/Mg refer to kilogram of carbon tetrachloride per megagram of flurocarbon 11 and 12 produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] One facility controls emissions from reactor venting with a vacuum jet, which removes HF and HCl from the emission stream, but not carbon tetrachloride.

[e] One facility controls emissions from the fluorocarbon 11 distillation vent with a condenser and carbon tetrachloride scrubber; carbon tetrachloride emissions result from the use of the scrubber.

[f] Reference 18.

[g] Reference 20.

[h] For the refrigerated condenser applied to storage emissions, the removal efficiency is based on an assumed uncontrolled emission temperature of 20°C and a condenser operating temperature of -15°C. Greater efficiency can be achieved by using a lower operating temperature.

NA - not applicable.

During mechanical maintenance operations, the fluorination reactor is vented through the HCl column accumulator, and at these times the vent stream contains carbon tetrachloride. The uncontrolled carbon tetrachloride emission factor for reactor venting is from reference 21. This reference did not indicate the frequency of reactor venting or the duration and emission rate associated with each such occurrence.

At one facility, a carbon tetrachloride scrubber is used to remove fluorocarbon emissions from the fluorocarbon 12 distillation vent (Vent B, Figure 6). The vent stream from the scrubber contains carbon tetrachloride. The emission rate for this source was 0.17 kg/hr at a fluorocarbon production rate of 7.6 Mg/hr.[18] The extent of the use of this control technique at other facilities is unknown.

Storage Emissions --

The uncontrolled emission factors for carbon tetrachloride feedstock storage in fixed roof tanks (Vents C, Figure 6) are from references 18 and 20.

Source Locations

A list of facilities producing fluorocarbons 11 and 12 is presented in Table 8.

TABLE 8. FACILITIES PRODUCING FLUOROCARBONS 11 AND 12[15,20,22,23]

Company	Location[a]
Allied Chemical Corp.[a]	Danville, IL El Segundo, CA
E.I. duPont de Nemours and Co., Inc.	Antioch, CA Deepwater, NJ Montague, MI
Essex Chemical Corp. (Racon Inc., Subsidiary)	Wichita, KS
Kaiser Aluminum and Chemical Corp.	Gramercy, LA
Penwalt Corp.	Calvert City, KY

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel.

CARBON TETRABROMIDE PRODUCTION

A small proportion of carbon tetrachloride is used as feedstock for the manufacture of carbon tetrabromide. Less than 25 Mg of carbon tetrabromide was produced in the United States in 1975.[2]

Process Description

Carbon tetrabromide is produced by a chlorine displacement process. In this process, carbon tetrachloride and anhydrous hydrogen bromide (HBr) are reacted in a series of batch reactors. Basic operations that may be used in the production of carbon tetrabromide by chlorine displacement are shown in Figure 7. Three reaction vessels are charged with a solution of aluminum tribromide catalyst in the starting chlorocarbon, which in the case of carbon tetrabromide production is carbon tetrachloride. Gaseous anhydrous HBr is fed into Reactor 1 below the liquid surface. Gas evolved from Reactor 1 is passed into the liquid in Reactor 2, and gas from Reactor 2 is passed into the liquid of Reactor 3. The gas from Reactor 3 is primarily hydrogen chloride and is vented to an acid scrubber. When the contents of Reactor 1 are sufficiently converted to carbon tetrabromide, the HBr stream is diverted to Reactor 2 and the contents of Reactor 1 are discharged for product recovery. The crude product is washed with water to remove the catalyst and is dried. Reactor 1 is then recharged with chlorocarbon and catalyst and becomes the third vessel in the reaction series.[24]

Emissions

Potential sources of carbon tetrachloride in the manufacture of carbon tetrabromide include the storage of carbon tetrachloride feedstock, the vent scrubber, and fugitive emissions. Insufficient information is available for the development of carbon tetrachloride emission factors for carbon tetrabromide production.

Source Locations

Table 9 lists companies and their locations that produce carbon tetrabromide.

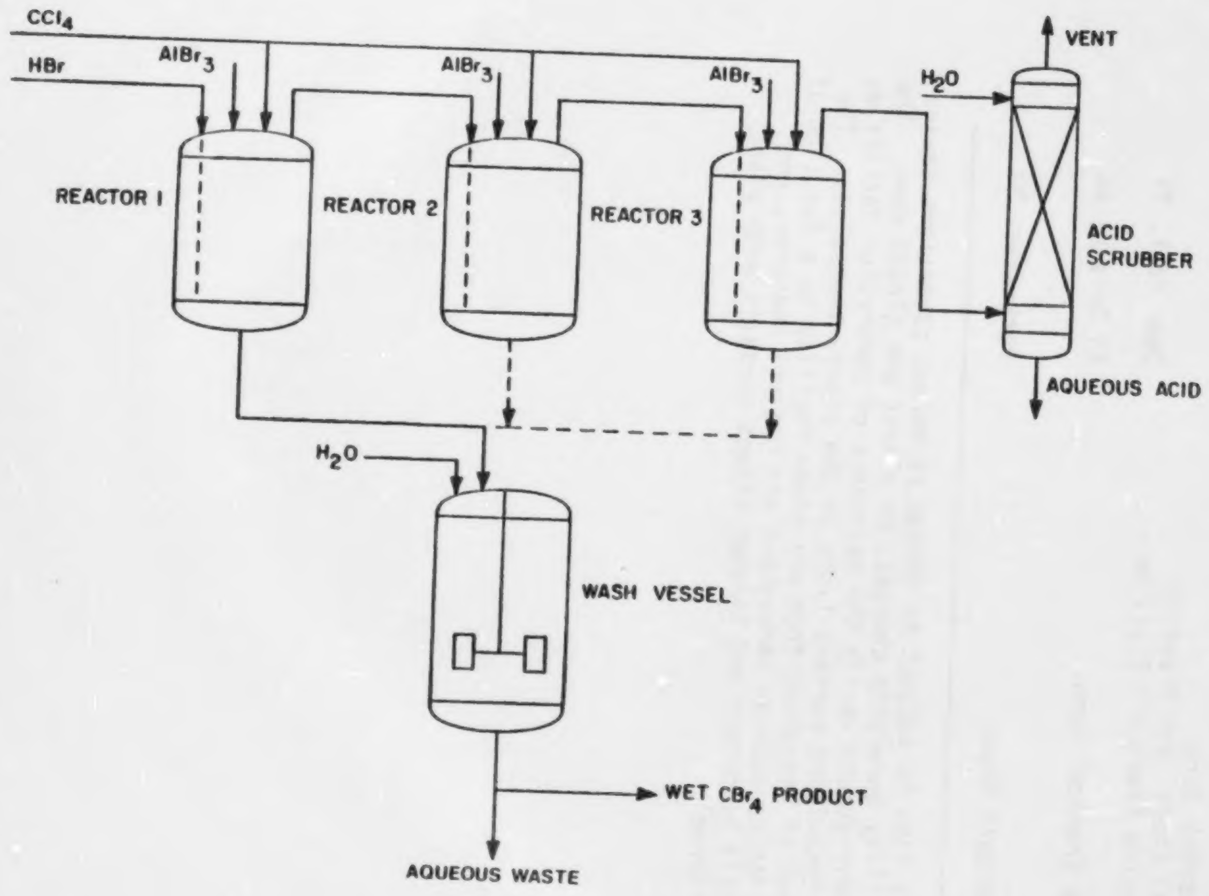

CCl_4
HBr
$AlBr_3$
$AlBr_3$
$AlBr_3$
VENT
H_2O
REACTOR I
REACTOR 2
REACTOR 3
ACID SCRUBBER
AQUEOUS ACID
H_2O
WASH VESSEL
WET CBr_4 PRODUCT
AQUEOUS WASTE

Figure 7. Basic operations that may be used in carbon tetrabromide production.[24]

TABLE 9. CARBON TETRABROMIDE PRODUCTION FACILITIES[15]

Plant	Location
Diamond Shamrock Corp. Industrial Chems. and Plastics Unit, Electro Chemicals Division	Deer Park, TX
Great Lakes Chemical Corp.	El Dorado, AK
Olin Corp. Olin Chemicals Group	Rochester, NY

NOTE: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves. The level of emissions from any given facility is a function of variables such as throughput and control measures, and should be determined through direct contacts with plant personnel.

LIQUID PESTICIDE FORMULATION

Carbon tetrachloride is used in a number of liquid pesticide formulations, primarily in fumigants. These formulations generally are mixtures of carbon tetrachloride and other active ingredients such as ethylene dibromide, sulfur dioxide, and carbon disulfide.[25]

Process Description

Pesticide formulation systems are typically batch mixing operations. Technical grade pesticide is usually stored in its original shipping container in the warehouse section of the plant until it is needed. If the material is received in bulk, it is transferred to holding tanks for storage. Solvents are normally stored in bulk tanks.[26]

Batch mixing tanks are typically closed vessels. The components of the formulation are fed into the tank, measured by weight, and mixed by circulation with a tank pump.[27] The formulated material is then pumped to a holding tank before being put into containers for shipment.[26]

The blend tank is vented to the atmosphere through a vent dryer, which prevents moisture from entering the tank.[27] Storage and holding tanks and container-filling lines are typically provided with an exhaust connection or hood to remove any vapors. The exhaust from the system is vented to a control device or directly to the atmosphere.[26]

Emissions

Sources of carbon tetrachloride emissions from pesticide formulation include storage vessels, mixing vessel vents, and leaks from pumps, valves, and flanges. Insufficient information is available for the development of carbon tetrachloride emission factors for liquid pesticide formulation facilities.

Source Locations

Registrants and applicants for registration of pesticidal products containing carbon tetrachloride are listed in Table 10. Some of the listed companies may buy a preformulated or prepackaged product from larger producers and therefore may not be actual sources of emissions. In addition, this list may change as facility ownership changes or plants are closed down.

TABLE 10. REGISTRANTS AND APPLICANTS FOR REGISTRATION OF PESTICIDAL PRODUCTS CONTAINING CARBON TETRACHLORIDE[25]

Company	Location
Southland Pearson & Co.	Mobile, AL
Cardinal Chemical Co.	San Francisco, CA
Coyne Chemical Co.	Los Angeles, CA
Hockwaldchem, Division of Oxford Chemicals	Brisbane, CA
Stauffer Chemical Co.	Richmond, CA
M.F. Canle & Co.	Tampa, FL
Dettelbach Chemicals Corp.	Atlanta, GA
Hill Manufacturing, Inc.	Atlanta, GA
Lester Laboratories	Atlanta, GA
Momar, Inc.	Atlanta, GA
Oxford Chemicals	Atlanta, GA
The Selig Chemical Industries	Atlanta, GA
Stephenson Chemical Co., Inc.	College Park, GA
Woolfolk Chemical Works, Inc.	Ft. Valley, GA
ZEP Manufacturing Co.	Atlanta, GA
Riverdale Chemical Co.	Chicago Heights, IL
Brayton Chemicals, Inc.	West Burlington, IA
MFA Oil Co.	Shenandoah, IA
Midland Laboratories, Inc.	Des Moines, IA
Bartels & Shores Chemical Co.	Kansas City, KS
Chemi Sol Chemicals & Sales Co.	Hutchison, KS
Industrial Fumigant Co.	Olathe, KS
PBI-Gordon Corp.	Kansas City, KS

CONTINUED

TABLE 10. (continued)

Company	Location
Research Products Co.	Salina, KS
Thompson-Hayward Chemical Co.	Kansas City, KS
Vulcan Materials Co., Chemicals Division	Wichita, KS
Weevil-cide Co.	Salina, KS
Grain Conditioners, Inc.	New Orleans, LA
Quinn Drug & Chemical Co.	Greenwood, MS
Dow Chemical USA	Midland, MI
Haertel Walter Co.	Minneapolis, MN
E.H. Leitte Co.	St. Paul, MN
Universal Cooperatives, Inc.	Minneapolis, MN
Douglas Chemical Co.	Liberty, MO
Farmland Industries, Inc.	Kansas City, MO
Ferguson Fumigants	Hazelwood, MO
The Huge Co., Inc.	St. Louis, MO
Knox Chemical Co.	St. Louis, MO
Patterson Chemical Co., Inc.	Kansas City, MO
Steward Sanitary Supply Co., Ltd.	St. Louis, MO
Techne Corp.	Kansas City, MO
Falls Chemicals, Inc.	Great Falls, MT
Warren-Douglas Chemical Co.	Omaha, NB
Agway, Inc., Chemical Division	Syracuse, NY
Prentis Drug & Chemical Co., Inc	New York, NY
Bernard Sirotta Co., Inc.	Brooklyn, NY

CONTINUED

TABLE 10. (continued)

Company	Location
West Chemical Products, Inc.	Lynbrook, NY
Lystad, Inc.	Grand Forks, ND
Diamond Shamrock Agricultural Chemicals	Cleveland, OH
Big F Insecticides, Inc.	Memphis, TN
Weil Chemicals Co.	Memphis, TN
J-Chem, A Division of Fumigators, Inc.	Houston, TX
Soweco, Inc.	Amarillo, TX
The Staffel Co.	San Antonio, TX
Atomic Chemical Co.	Spokane, WA

Note: The companies listed are registrants of pesticidal products containing carbon tetrachloride. Some of these companies may buy a performulated or prepackaged product and, therefore may not be actual sources of emissions. In addition, the list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel.

PHARMACEUTICAL MANUFACTURING

Carbon tetrachloride is used as a solvent in the manufacturing of pharmaceutical products by chemical synthesis.[28]

Process Description

Synthetic pharmaceuticals are normally manufactured in a series of batch operations, many of which involve the use of solvents. Figure 8 presents basic operations that may be used in a batch synthesis process. To begin a production cycle, the reactor is water washed and dried with a solvent. Air or nitrogen is usually used to purge the tank after it is cleaned. Solid reactants and solvent are then charged to the reactor. After the reaction is complete, any remaining unreacted volatile compounds and solvents are removed from the reactor by distillation and condensed. The pharmaceutical product is then transferred to a holding tank. In the holding tank, the product may be washed three to four times with water or solvent to remove any remaining reactants and byproducts. The solvent used in washing generally is evaporated from the reaction product. The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification. After crystallization, the solid material is separated from the remaining solvent by centrifuging. While in the centrifuge, the product cake may be washed several times with water or solvent. Tray, rotary, or fluid-bed dryers are employed for final product finishing.[28]

Emissions

Where carbon tetrachloride is used as a solvent in the manufacture of a pharmaceutical product, each step of the manufacturing process may be a source of carbon tetrachloride emissions. The magnitude of emissions varies widely within and among operations; therefore. it is impossible to cite typical emission rates for various operations. Based on an industry wide mass balance,[28] at the current level of control, about 11 percent of the carbon tetrachloride used in the industry is emitted to the air. Thus, the industry-wide controlled emission factor is about 110 kilograms per megagram of carbon tetrachloride used.

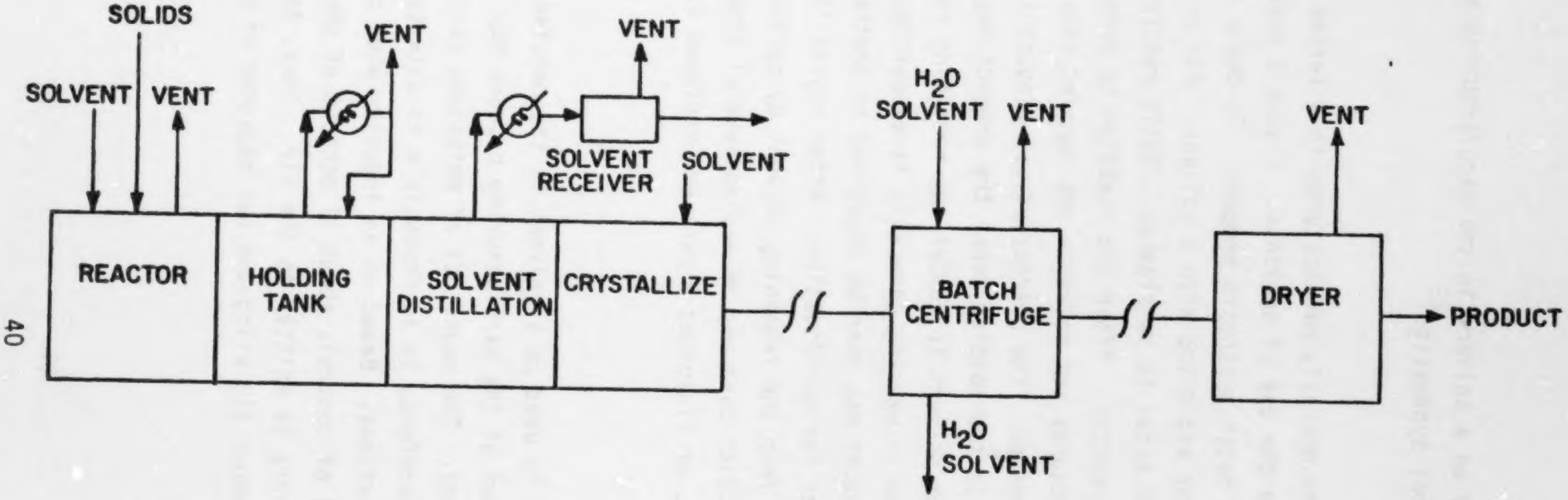

SOLIDS
SOLVENT
VENT
VENT
VENT
SOLVENT RECEIVER
SOLVENT
REACTOR
HOLDING TANK
SOLVENT DISTILLATION
CRYSTALLIZE
H_2O SOLVENT
VENT
BATCH CENTRIFUGE
H_2O SOLVENT
VENT
DRYER
PRODUCT

Figure 8. Basic operations that may be used in synthetic pharmaceutical manufacturing.[28]

An approximate ranking of emission sources has been established and is presented below in order of decreasing emission significance. The first four sources typically account for the majority of emissions from a plant.[28]

1. Dryers
2. Reactors
3. Distillation units
4. Storage and transfer
5. Filters
6. Extractors
7. Centrifuges
8. Crystallizers

Condensers, scrubbers, and carbon adsorbers can be used to control emissions from all of the above emission sources. Storage and transfer emissions can also be controlled by the use of vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks.[28]

Source Locations

The Standard Industrial Classification (SIC) code for pharmaceutical preparations is 2834. There are approximately 800 pharmaceutical plants producing drugs in the United States and its territories. Most of the plants are small and have less than 25 employees. Nearly 50 percent of the plants are located in 5 States: 12 percent in New York, 12 percent in California, 10 percent in New Jersey, 5 percent in Illinois, and 6 percent in Pennsylvania. These States also contain the largest plants in the industry. Puerto Rico has had the greatest growth in the past 15 years, during which 40 plants have located there. Puerto Rico now contains 90 plants or about 7.5 percent of the total. EPA's Region II (New Jersey, New York, Puerto Rico, Virgin Islands) has 340 plants (28 percent of the total); Region V (Illinois, Minnesota, Michigan, Ohio, Indiana, Wisconsin), 215 plants (20 percent); and Region IX (Arizona, California, Hawaii, Guam, American Samoa), 143 plants (13 percent).[28]

USE OF PESTICIDES CONTAINING CARBON TETRACHLORIDE

The primary use of carbon tetrachloride in pesticides is as a component of fumigant mixtures. These fumigants are applied to control insect infestations in grains during storage, transfer, milling, distribution, and processing.[25] It has been estimated that 98 percent of liquid fumigant formulations containing carbon tetrachloride is used on stored grain while 2 percent is used in the fumigation of grain mill equipment.[29]

Carbon tetrachloride is used in over 98 percent of the grain fumigant mixtures available for application to stored grain.[30] Other ingredients of these mixtures include ethylene dibromide, ethylene dichloride, sulfur dioxide, and carbon disulfide. The most common grain fumigant formulations are:

- Carbon tetrachloride 80 percent, carbon disulfide 20 percent;
- Carbon tetrachloride 80.9 percent, carbon disulfide 16 percent, ethylene dibromide 1.2 percent, sulfur dioxide 1.5 percent, and pentane 0.4 percent;
- Carbon tetrachloride 77 percent, carbon disulfide 15.4 percent, ethylene dibromide 5 percent, sulfur dioxide 1.5 percent, and pentane 0.4 percent;
- Carbon tetrachloride 60 percent, ethylene dichloride 35 percent, and ethylene dibromide 5 percent; and
- Carbon tetrachloride 75 percent, ethylene dichloride 25 percent.

Table 11 lists brand names of fumigant products containing carbon tetrachloride.

Carbon tetrachloride fumigant formulations are used at farms; at off-farm grain elevators including subterminal, terminal. and port elevators; at mill holding facilities; and in transport vehicles. In 1977-78, 3.6 million liters of fumigants containing 3,900 Mg of carbon tetrachloride were applied to grains stored on farms, while 7.6 million liters containing 8,900 Mg of carbon tetrachloride were used at off-farm facilities. Carbon tetrachloride formulations are more widely used at smaller grain elevators than at large elevators. About 70 percent of the grain stored at large grain elevators such as terminal elevators are treated with aluminum phosphide formulations, which do not include carbon tetrachloride.[29]

TABLE 11. CARBON TETRACHLORIDE FUMIGANT BRAND NAMES[25]

Acritet 34-66

Agway Serafume

Big F "LGF" Liquid Gas Fumigant

Best 4 Servis Brand 75-25 Standard Fumigant

Brayton 75-25 Grain Fumigant

Brayton Flour Equipment Fumigant for Bakeries

Brayton EB-5 Grain Fumigant

Bug Devil Fumigant

Cardinal Fume

Chemi-Fume Fumigant Type B

Co-op Activated 80-20 Grain Fumigant Fire Inhibited

Co-op New Activated Weevil Killer Fumigant

Crest 15 Grain Fumigant

De-Pester Weevil Kill

De Pester Fumigant No. 2

De-Pester Grain Conditioner and Weevil Killer

De Pester Super Fumigas

De-Pester Fumigant No. 1

De-Pester Fumigant 82 FR

Diamond 75-25 Grain Fumigant

Diweevil

Douglas Tetrafume Weevile Killer & Grain Conditioner

Douglas Tetrakil Weevil Killer and Grain Conditioner

Douglas Suffokato #3 Grain and Mill Spot Fumigant

CONTINUED

TABLE 11. (continued)

Douglas Tetrakote Liquid Grain Protectant
Douglas Topkote #77 Insect Killer
Douglas Grainkote
Douglas Proteckote
Dowfume EB-15 Inhibited
Dowfume 75
Dowfume EB-5 Effective Grain Fumigant
Dowfume C
Dowfume F
Dowfume EB-59
Dow Vertifume S
Dynafume
Excelcide Excelfume
Extrafume
FC-14 Formula 82-H Grain Fumigant 80-20 Mixture
FC-7 Grain Fumigant
FC-4 SX Grain Storage Fumigant
FC-13 Mill Machinery Fumigant
F.1.A. "80-20" Grain Fumigant
Fire Retarded Millfume No. 1 Grain Fumigant with Sulfur Dioxide
Formula 815 (FC-3) Grain Fumigant
Formula 635 (FC-2) Grain Fumigant
Fume-O-Death Gas No. 3
Fumisol

CONTINUED

TABLE 11. (continued)

Gar-be-cide Special Mill Spray
Gas-o-cide
Grainex New Grain Fumigant
Grain Fumigant
Grainfume MB
Hill's Hilcofume 75
Hydrochlor Fumigant
Hydrochlor GF Liquid Gas Fumigant
Infuco 80-20 with 502 Grain Fumigant
Infuco 80-20 Grain Fumigant
Infuco Bin-fume Grain Fumigant
Infuco 50-50 Spot Fumigant
Infuco Two-in-One Grain Fumigant
Infuco Fumigant 75
Iso-Fume
J-Fume-20
J-Fume 80-20
J-Fume-75
J-Fume-C
J-Fume 80-20 Liquid Grain Fumigant
Larvaracide 15 Liquid Grain Fumigant
Leitte Spotfume 60
M.F.A. Inhibited 80-20 Plus
Max Spot Kill Machinery Fumigant

CONTINUED

TABLE 11. (continued)

Max Kill 10 Liquid Grain Fumigant
Max Kill High Life Liquid Grain Fumigant
Max Kill 75-25
Max Kill Spot - 59 Spot Fumigant for Mills and Milling Machinery
Momar Mill-X Fumigant
Momar Grain-Guard Grain Protectant in Liquid Form
Parson Lethogas Fumigant
Patterson's Weevil Killer
Pearson's Fumigrain P-75
Pioneer Brand Grain Fumigant
Proteckote
Riverdale Fumigant
Selig's Grainfume
Selig's Selcofume
Selig's Grain Fumigant No. 15
Selig's Grain Storage Fumigant
Serfume
Sirotta's Sircofume Liquid Fumigating Gas
Spray-Trol Brand Insecticide Fumi-Trol
Spot Fumigant
Standard 75-25 Fumigant
Staffel's Grain Fumigant
Stauffer 80-20 Grain Fumigant
Stauffer Chemicals F.I.A. "80-20"

CONTINUED

TABLE 11. (continued)

Grain Fumigant with SO_2
Stephenson Chemicals Stored Grain Fumigant
Stephenson Sure-Guard Brand Liquid Grain Protectant and Fumigant
Sure Death Brand Millfume "66"
Sure Death Brand Millfume No. 2
T-H Vault Fumigant
T-H Grain Fumigant No. 7 Weevil Killer and Grain Conditioner
Terminal Grain Fumigant (FC-15)
Toxi-Fog
Trifume A Grain Fumigant
Unico Premium Grain Fumigant
Vertifume
Vulcan Formula 635 (FC-2) Grain Fumigant
Vulcan Formula 72 Grain Fumigant
Waco-50
Warlasco Grain Fumigant No. 3
Wasco Grain Fumigant
Weevil-Cide
914 Weevil Killer and Grain Conditioner
Zep-O-Fume Grain Mill Fumigant

Process Description

Liquid grain fumigants are used on approximately 12 percent of the grain grown in the United States. Fumigants are used during binning (placement in storage) and turning (shifting from one storage facility to another) operations and at other times during storage when infestation occurs. Fumigants have a period of effectiveness of only a few days. Thus, they kill existing insect populations but do not prevent later reinfestation. Newly harvested grain typically is fumigated 6 weeks after binning. Corn grown in the southern regions of the U.S. usually is fumigated immediately following binning because of field infestation by weevils.[31]

A variety of structures are used for grain storage. Farm grain storage facilities are mostly metal with some wooden bins of flat, older, and loose-fitting construction. Country elevators are of two types: small banked concrete silos and flat storages. At mills, banked silos are predominant. Terminal elevators are banked silos. Grain transportation vehicles include trucks, rail cars (box, freight, hopper), inland barges, ocean barges, and ships. Subterminal and terminal elevators and shipholds are usually almost air tight, while farm grain storage facilities generally allow considerable air flow.[30,31] On-farm facilities typically have a capacity of about 3,000 bushels, while country elevators using carbon tetrachloride fumigants have a capacity of about 300,000 bushels. Terminal elevators have an average capacity of 4 million bushels.[31]

Grain fumigants are applied primarily by the "gravity distribution" method by either surface application or layering. This method is practiced both on-farm and off-farm. A second method of fumigant application is "outside of car" application, where the fumigant is either poured from 1- or 5-gallon containers through vents located in the roof of the car or sprayed into the car with a power sprayer.[25]

Equipment used to apply fumigants includes common garden sprinkling cans with spray heads removed; 3- to 5-gallon capacity compressed air sprayers from which the nozzles have been removed; high capacity motor driven pumps to apply large volumes of liquid materials directly from large drums; metering devices to treat streams of moving grain; and distribution tube and pressure reduction valve systems for discharging of liquids stored under pressure.[31]

The rate of application of fumigants is dependent on the type of grain and the type of storage facility. Table 12 presents general application rates for various types of grain for both on-farm and off-farm storage. The application rates for off-farm storage are lower since these types of facilities are typically more tight-fitting than on-farm storage.[30]

After application of fumigants, grain generally is left undisturbed for at least 72 hours. The usual practice is to leave the grain for a much longer period. Fumigants are often left on the grain until the normal turning procedure is undertaken. Alternatively, the grain may be aerated by turning after completion of the required treatment period. In tight-fitting facilities equipped with recirculation or forced distribution blowers, the fumigant is ventilated from the grain with fresh air by operating the blowers for 3 to 4 hours.[31]

Emissions

Emissions of carbon tetrachloride from fumigant mixtures will occur during fumigant application and when fumigated grain is exposed to the atmosphere, for instance, during turning or loading. Because of the relatively high vapor pressure of carbon tetrachloride, it is estimated that essentially all carbon tetrachloride used in fumigants evaporates. However, the time rate of emissions is highly variable and depends on the application rate, the type of storage (whether loose or tight-fitting), the manner in which the grain is handled, and the rate of release of fumigant residues on and in the grain. Figure 9 presents the results of a laboratory study of the level of residual carbon tetrachloride fumigant on wheat as a function of the number of days since aeration.[32] The grain was fumigated and aerated under conditions comparable to commercial fumigation and aeration conditions.[25]

Source Locations

The Standard Industrial Classification (SIC) codes for farms at which grain may be stored are as follows:

TABLE 12. FUMIGANT APPLICATION RATES[30]

Grain	Application rate (gal/10^3 bu) On-farm	Application rate (gal/10^3 bu) Off-farm
Wheat	3 - 4	2 - 3
Corn	4 - 5	3 - 4
Rice, Oats, Barley, Rye	3 - 4	2 - 3
Grain sorghum	5 - 6	4 - 5

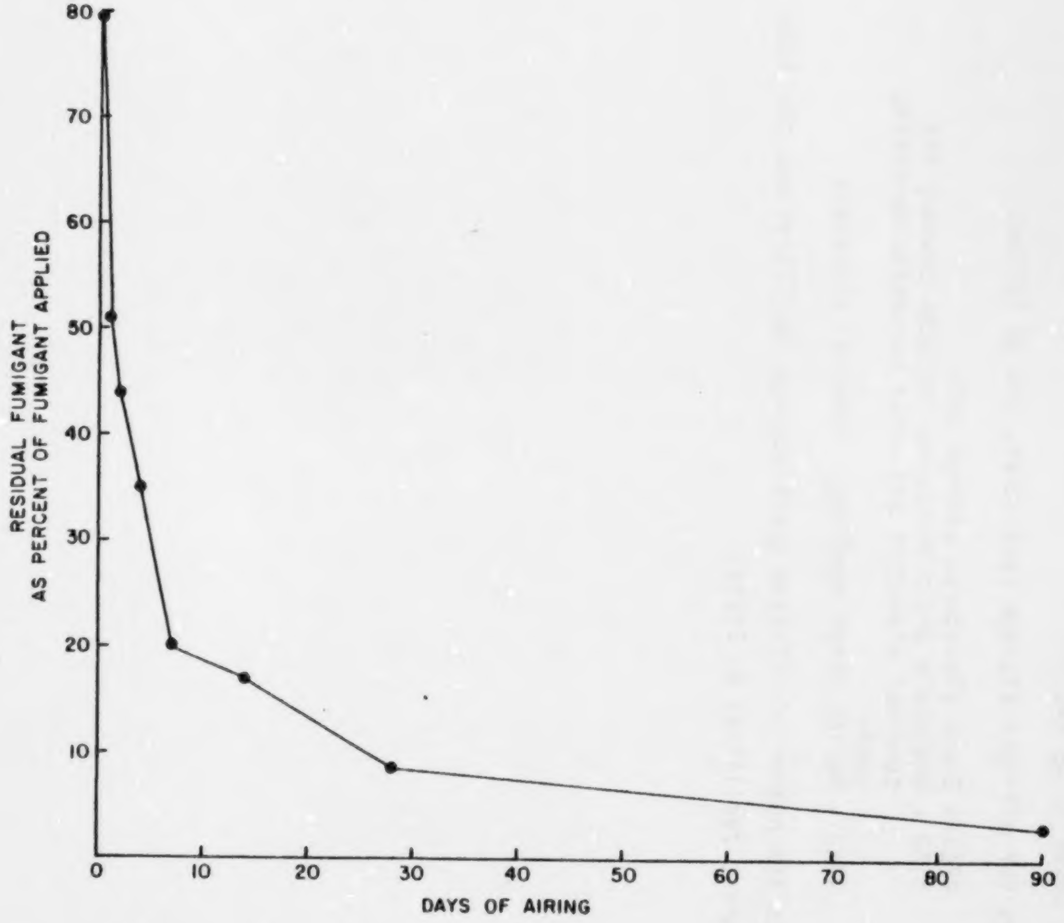


Figure 9. Residual carbon tetrachloride fumigant as a function of the number of days grain is aired.[32]

0111 - Agricultural production of wheat
0112 - Agricultural production of rice
0115 - Agricultural production of corn
0116 - Agricultural production of soybeans
0119 - Agricultural production of other grains
0191 - General farms

Table 13 lists the on-farm grain storage capacity by State and the percentage of total U.S. capacity by region.

SIC codes for off-farm storage facilities, are as follows:

4221 - Grain elevators, storage only
5153 - Wholesale grain merchants includes country and terminal elevators and other merchants marketing grain
4463 - Marine cargo handling - terminal elevators.

Table 14 lists the number of off-farm grain storage facilities and the total capacity of these facilities by State.

TABLE 13. ON-FARM GRAIN STORAGE[29]

Region and State	Capacity (10^3 bu)	Regional percentage	
Northeast:	142,698	2%	
Maine	2,866		
New Hampshire	0		
Vermont	0		
Massachusetts	9,654		
Rhode Island	0		
Connecticut	222		
New York	39,204		
New Jersey	5,190		
Pennsylvania	62,498		
Delaware	2,057		
Maryland	21,007		
Lake States:	1,357,597	17%	
Michigan	116,462		
Wisconsin	244,827		
Minnesota	996,338		
Corn Belt:	2,982,755	37%	80%
Ohio	225,279		
Indiana	429,981		
Illinois	947,208		
Iowa	1,071,203		
Missouri	309,084		
Northern Plains:	2,132,264	26%	
North Dakota	681,397		
South Dakota	394,381		
Nebraska	715,594		
Kansas	340,892		
Appalachian:	236,607	3%	
Virginia	37,554		
West Virginia	5,685		
North Carolina	100,938		
Kentucky	49,237		
Tennessee	43,193		
Southeast:	159,132	2%	
South Carolina	31,437		
Georgia	87,720		
Florida	12,145		
Alabama	27,830		

CONTINUED

TABLE 13. (continued)

Region and State	Capacity (10^3 bu)	Regional percentage
Delta States:	131,593	1%
Mississippi	41,588	
Arkansas	50,095	
Louisiana	39,910	
Southern Plains:	315,160	4%
Oklahoma	76,685	
Texas	238,472	
Mountain:	507,357	6%
Montana	278,783	
Idaho	77,960	
Wyoming	19,519	
Colorado	97,216	
New Mexico	9,136	
Arizona	6,404	
Utah	15,220	
Nevada	3,119	
Pacific:	151,622	2%
Washington	60,011	
Oregon	33,552	
California	58,059	
Total	8,116,815	100%

TABLE 14. OFF-FARM GRAIN STORAGE[29]

State	Number of facilities	Capacity (10^3 bu)
Alabama	37,290	178
Arizona	33,890	76
Arkansas	179,180	283
California	115,710	226
Colorado	91,500	209
Delaware	17,200	27
Florida	6,070	27
Georgia	56,700	344
Idaho	64,070	231
Illinois	775,260	1,177
Indiana	245,550	804
Iowa	635,000	1,141
Kansas	830,000	1,086
Kentucky	49,580	202
Louisiana	87,010	131
Maryland	36,940	64
Michigan	90,240	351
Minnesota	366,440	894
Mississippi	76,350	183
Missouri	204,140	611
Montana	54,000	298
Nebraska	484,600	740
Nevada	300	4
New Jersey	2,200	24
New Mexico	17,550	27
New York	70,270	243
North Carolina	63,420	465
North Dakota	140,070	580
Ohio	228,800	713
Oklahoma	203,520	400
Oregon	65,530	238
Pennsylvania	26,900	337
South Carolina	33,470	177
South Dakota	83,820	386
Tennessee	43,180	106
Texas	720,350	896
Utah	17,170	55
Virginia	29,920	241
Washington	186,370	324
West Virginia	530	9
Wisconsin	118,920	428
Wyoming	5,580	49
Other States	5,170	80
Total	6,600,030	15,065

ETHYLENE DICHLORIDE PRODUCTION

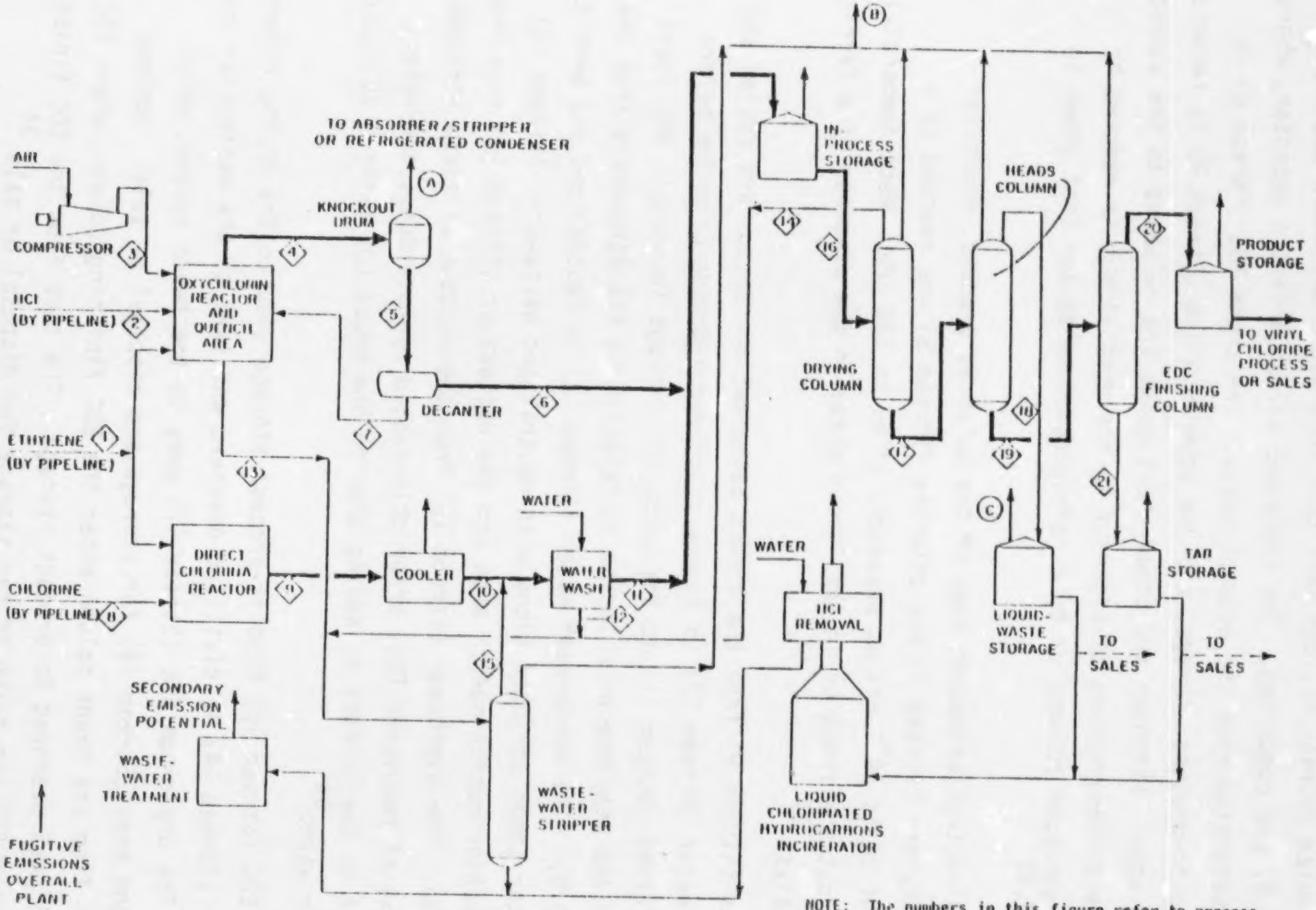
Carbon tetrachloride is formed as a byproduct during the production of ethylene dichloride (EDC). Ethylene dichloride is produced from ethylene and chlorine by direct chlorination, and ethylene and hydrogen chloride (HCl) by oxychlorination. At most production facilities, these processes are used together in what is known as the balanced process. This section discusses carbon tetrachloride emissions from this process.

The balanced process generally is used wherever EDC and vinyl chloride monomer (VCM) are produced at the same facility. About 81 percent of the EDC produced domestically is used in the manufacture of VCM.[33] In VCM production, EDC is dehydrochlorinated to yield VCM and byproduct HCl. In the balanced process, byproduct HCl from VCM production via the direct chlorination/dehydrochlorination process is used in the oxychlorination/dehydrochlorination process.

Process Description

The balanced process consists of an oxychlorination operation, a direct chlorination operation, and product finishing and waste treatment operations. The raw materials for the direct chlorination process are chlorine and ethylene. Oxychlorination involves the treatment of ethylene with oxygen and HCl. Oxygen for oxychlorination generally is added by feeding air to the reactor, although some plants use purified oxygen as feed material.[34]

Basic operations that may be used in a balanced process using air for the oxychlorination step are shown in Figure 10. Actual flow diagrams for production facilities will vary. The process begins with ethylene (Stream 1) being fed by pipeline to both the oxychlorination reactor and the direct chlorination reactor. In the oxychlorination reactor the ethylene, anhydrous hydrogen chloride (Stream 2), and air (Stream 3) are mixed at molar proportions of about 2:4:1, respectively, producing 2 moles of EDC and 2 moles of water. The reaction is carried out in the vapor phase at 200 to 315°C in either a fixed-bed or fluid-bed reactor. A mixture of copper chloride and other chlorides is used as a catalyst.[34]


AIR
COMPRESSOR
HCl (BY PIPELINE)
ETHYLENE (BY PIPELINE)
CHLORINE (BY PIPELINE)
OXYCHLORIN REACTOR AND QUENCH AREA
DIRECT CHLORINA REACTOR
TO ABSORBER/STRIPPER OR REFRIGERATED CONDENSER
A
KNOCKOUT DRUM
DECANTER
COOLER
WATER
WATER WASH
WASTE-WATER STRIPPER
SECONDARY EMISSION POTENTIAL
WASTE-WATER TREATMENT
FUGITIVE EMISSIONS OVERALL PLANT
B
IN-PROCESS STORAGE
DRYING COLUMN
HEADS COLUMN
EDC FINISHING COLUMN
PRODUCT STORAGE
TO VINYL CHLORIDE PROCESS OR SALES
WATER
HCl REMOVAL
LIQUID CHLORINATED HYDROCARBONS INCINERATOR
C
LIQUID-WASTE STORAGE
TAR STORAGE
TO SALES
TO SALES
1
2
3
4
5
6
7
8
9
10
11
12
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19
20
21

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 10. Basic operations that may be used in the production of ethylene dichloride by the balanced process, with air-based oxychlorination.[34]

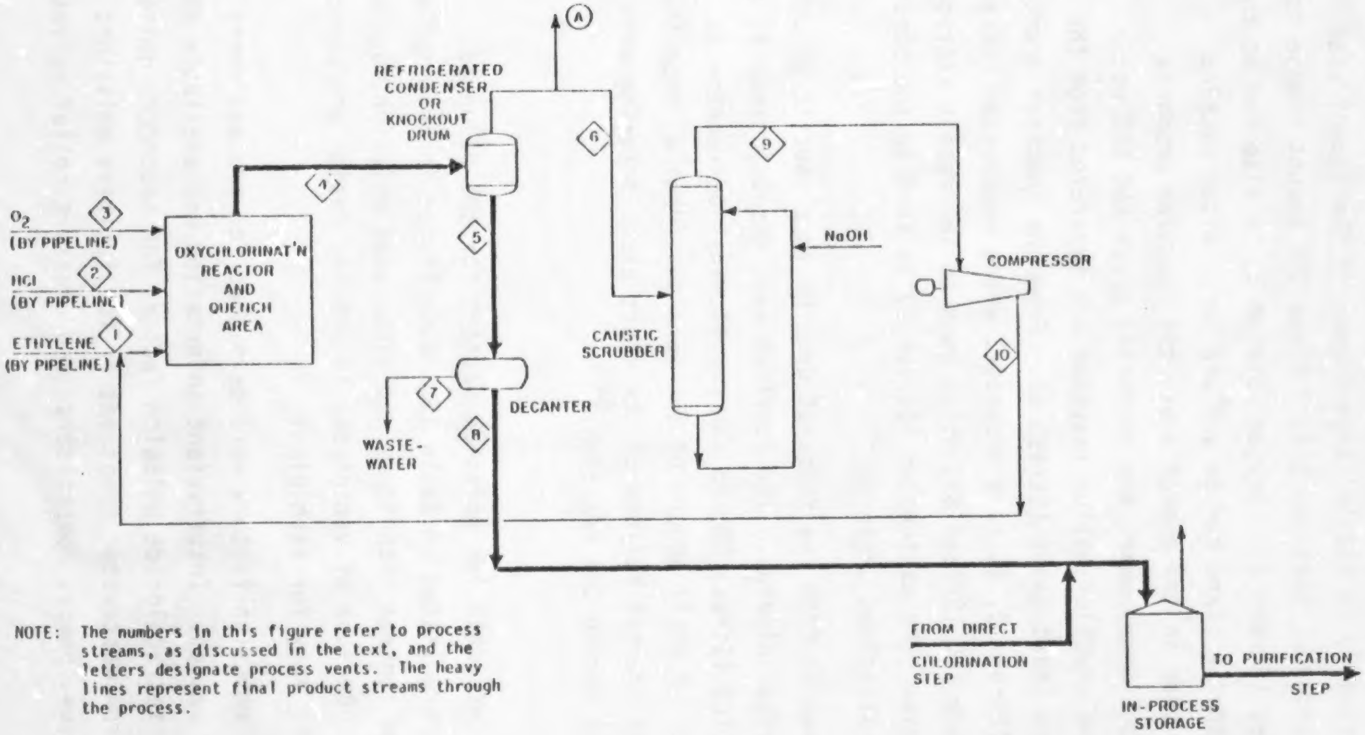
The products of reaction from the oxychlorination reactor are quenched with water, cooled (Stream 4), and sent to a knockout drum, where EDC and water (Stream 5) are condensed. The condensed stream enters a decanter, where crude EDC is separated from the aqueous phase. The crude EDC (Stream 6) is transferred to in-process storage, and the aqueous phase (Stream 7) is recycled to the quench step. Nitrogen and other inert gases are released to the atmosphere (Vent A). The concentrations of organics in the vent stream is reduced by absorber and stripper columns or by a refrigerated condenser (not shown in Figure 10).[27,34]

In the direct-chlorination step of the balanced process, equimolar amounts of ethylene (Stream 1) and chlorine (Stream 8) are reacted at a temperature of 38 to 49^{o}C and at pressures of 69 to 138 kPa. Most commercial plants carry out the reaction in the liquid phase in the presence of a ferric chloride catalyst.[34]

Products (Stream 9) from the direct chlorination reactor are cooled and washed with water (Stream 10) to remove dissolved hydrogen chloride before being transferred (Stream 11) to the crude EDC storage facility. Any inert gas fed with the ethylene or chlorine is released to the atmosphere from the cooler (Vent B). The waste wash water (Stream 12) is neutralized and sent to the wastewater steam stripper along with neutralized wastewater (Stream 13) from the oxychlorination quench area and the wastewater (Stream 14) from the drying column. The overheads (Stream 15) from the wastewater steam stripper, which consist of recovered EDC, other chlorinated hydrocarbons, and water, are returned to the process by adding them to the crude EDC (Stream 10) going to the water wash.[34]

Crude EDC (Stream 16) from in-process storage goes to the drying column, where water (Stream 14) is distilled overhead and sent to the wastewater steam stripper. The dry crude EDC (Stream 17) goes to the heads column, which removes light ends (Stream 18) for storage and disposal or sale. Bottoms (Stream 19) from the heads column enter the EDC finishing column, where EDC (Stream 20) goes overhead to product storage. The tars from the EDC finishing column (Stream 21) are taken to tar storage for disposal or sale.[34]

Several domestic EDC producers use oxygen as the oxidant in the oxychlorination reactor. Figure 11 shows basic operations that may be used in an oxygen-based oxychlorination process as presented in the literature. For


O2
(BY PIPELINE)
HCl
(BY PIPELINE)
ETHYLENE
(BY PIPELINE)
1
2
3
OXYCHLORINAT'N REACTOR AND QUENCH AREA
4
REFRIGERATED CONDENSER OR KNOCKOUT DRUM
A
5
6
7
8
9
10
WASTE-WATER
DECANTER
CAUSTIC SCRUBBER
NaOH
COMPRESSOR
FROM DIRECT CHLORINATION STEP
IN-PROCESS STORAGE
TO PURIFICATION STEP

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 11. Basic operations that may be used in the production of ethylene dichloride by the balanced process, oxygen-based oxychlorination step.[34]

a balanced process plant, the direct chlorination and purification steps are the same as those shown in Figure 10, and, therefore, are not shown again in Figure 11. Ethylene (Stream 1) is fed in large excess of the amount used in the air oxychlorination process, that is, 2 to 3 times the amount needed to fully consume the HCl feed (Stream 2). Oxygen (Stream 3) is also fed to the reactor, which may be either a fixed bed or a fluid bed. After passing through the condensation step in the quench area, the reaction products (Stream 4) go to a knockout drum, where the condensed crude EDC and water (Stream 5) produced by the oxychlorination reaction are separated from the unreacted ethylene and the inert gases (Stream 6). From the knockout drums the crude EDC and water (Stream 5) go to a decanter, where wastewater (Stream 7) is separated from the crude EDC (Stream 8), which goes to in-process storage as in the air-based process. The wastewater (Stream 7) is sent to the steam stripper for recovery of dissolved organics.[34]

The vent gases (Stream 6) from the knockout drum go to a caustic scrubber for removal of HCl and carbon dioxide. The purified vent gases (Stream 9) are then compressed and recycled (Stream 10) to the oxychlorination reactor as part of the ethylene feed. A small amount of the vent gas (Vent A) from the knockout drum is purged to prevent buildup of the inert gases entering with the feed streams or formed during the reaction.[34]

Emissions

Uncontrolled carbon tetrachloride emission factors for the balanced process of EDC production are listed in Table 15. Also listed in this table are potentially applicable control techniques and associated emission factors for controlled emissions. Because of variations in process design and age of equipment, actual emissions vary for each plant.

Carbon tetrachloride emission factors were developed for process vents and the storage of liquid wastes. Insufficient information was available for the calculation of carbon tetrachloride emission factors for secondary emissions of carbon tetrachloride from wastewater treatment or for fugitive emissions from leaks in process valves, pumps, compressors, and pressure relief valves.

TABLE 15. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS FOR A HYPOTHETICAL FACILITY PRODUCING ETHYLENE DICHLORIDE BY THE BALANCED PROCESS[a]

Emission source	Source designation[b]	Uncontrolled carbon tetrachloride emission factor (kg/Mg)[c]	Potentially applicable control technique[d]	% reduction	Controlled carbon tetrachloride emission factor (kg/Mg)[c]
Oxychlorination vent					
Air process	A	0.29 to 1.2	Thermal oxidizer	98+	$\leq 5.8\times10^{-3}$ to 2.4×10^{-2}
Oxygen process	A	0.044 to 0.18	Thermal oxidizer	98+	$\leq 8.8\times10^{-4}$ to 3.6×10^{-3}
Column vents	B	0.14	Thermal oxidizer	98+	$\leq 2.8\times10^{-3}$
Liquid waste storage	C	0.0051	Refrigerated condenser	85	7.7×10^{-4}

[a] Any given EDC production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Letters refer to vents designated to Figure 10, except for the oxygen-based oxychlorinator vent which is shown in Figure 11.

[c] Emission factors in terms of kg/mg refer to kilogram of carbon tetrachloride emitted per megagram of EDC produced by the balanced process. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] The control efficiency for incineration varies depending on the design of the incinerator and the compound which is burned. The 98 percent level is an estimate of the control efficiency on an incinerator with a residence time of about 0.75 seconds and a temperature of about 870°C, for a compound which is difficult to incinerate. Incinerators operating at longer residence times and higher temperatures may achieve higher efficiences.[43] Refrigerated condenser as control technique for emissions from liquid waste storage and associated reduction of 85% from reference 34.

Process Emissions --

Carbon tetrachloride process emissions originate from the purging of inert gases from the oxychlorination vent (Vent A, Figures 10 and 11) and from the release of gases from the column vents (Vent B, Figure 10), primarily the heads column. Carbon tetrachloride was not detected in an emissions test of a direct chlorination vent.[35]

The range of emission factors for the oxychlorination vent in the air based process was determined from carbon tetrachloride emission rates and associated EDC production rates reported by three facilities. The lowest emission factor, 0.29 kg/Mg, was calculated from a carbon tetrachloride emission rate of 14,000 kg/yr[36] and an associated EDC production rate of 50,000 Mg/yr.[37] The highest emission factor, 1.2 kg/Mg, was calculated from a carbon tetrachloride emission rate of 116,000 kg/yr and an associated EDC production rate of 99,800 Mg/yr.[38] An intermediate value, 0.42 kg/Mg, was calculated from a carbon tetrachloride emission rate of 35,000 kg/yr[39] and an EDC production rate of 83,000 Mg/yr.[40]

Data on the carbon tetrachloride concentration in the oxychlorination vent emissions from the oxygen-based process were not available; therefore, the emission factor for this process was calculated using emission composition data from the air-based process. It was assumed that the percentage of carbon tetrachloride in total chlorinated hydrocarbon emissions is the same for the air-based and oxygen-based processes. However, according to composition data for oxychlorination vent emissions for hypothetical plants of the two processes, chlorinated hydrocarbons are a smaller component of total VOC in the oxygen-based process (9.6 percent) than in the air-based process (64 percent).[34] Thus, the ratio of these two percentages (0.15) was used to account for the smaller proportion of chlorinated hydrocarbons in the emissions from the oxygen-based process.

The emission factor for the column vents (Vent B, Figure 6) was based on a published carbon tetrachloride emission factor for the heads column of 0.30 kg of carbon tetrachloride emitted per Mg EDC produced by oxychlorination.[41] The carbon tetrachloride emission factor for the balanced process was calculated by multiplying by the hypothetical plant EDC production by oxychlorination of 46.3 percent of total EDC production.[34]

Many plants incinerate vent gases from the oxychlorination reactor and column vents to reduce atmospheric emissions of volatile organics. This includes plants using the air-based as well as the oxygen-based oxychlorination processes.[42] Thermal oxidation is estimated to reduce chloroform emissions by 98 percent or greater. Incineration destruction efficiency varies with emission stream properties and incinerator operating parameters. The 98 percent efficiency level is based on incinerator operation at 870°C and 0.75 second residence time for a compound which is difficult to incinerate.[43] The emission reduction may be greater for longer residence times or higher operating temperatures.

Storage Emissions --

The uncontrolled carbon tetrachloride emission factor for the storage of waste-liquid light ends (Vent D, Figure 10) was calculated from a VOC emission factor of 0.030 kg/Mg.[34] It was assumed that the gaseous emissions from this source have the same concentration of carbon tetrachloride as the light ends (17 percent).[44]

Source Locations

Major EDC producers and production locations are listed in Table 16.

TABLE 16. ETHYLENE DICHLORIDE PRODUCTION FACILITIES[15,27]

Manufacturer	Location
Atlantic Richfield Co. ARCO Chem. Co., div.	Port Arthur, TX
Diamond Shamrock	Deer Park, TX
Dow Chem. U.S.A.	Freeport, TX Oyster Creek, TX Plaquemine, LA
E.I. duPont de Nemours & Co., Inc. Conoco Inc., subsid. Conoco Chems. Co. Div.	Lake Charles, LA
Ethyl Corp. Chems. Group	Baton Rouge, LA Pasadena, TX
Formosa Plastics Corp., U.S.A.	Baton Rouge, LA Point Comfort, TX
Georgia-Pacific Corp. Chem. Div.	Plaquemine, LA
The BF Goodrich Co. BF Goodrich Chem. Group	La Porte, TX Calvert City, KY Convent, LA
PPG Indust., Inc. Indust. Chem. Div.	Lake Charles, LA
Shell Chem. Co.	Deer Park, TX
Union Carbide Corp. Ethylene Oxide Derivatives Div.	Taft, LA Texas City, TX
Vulcan Materials Co. Vulcan Chems., div.	Geismar, LA

Note: This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel.

PERCHLOROETHYLENE AND TRICHLOROETHYLENE PRODUCTION

Carbon tetrachloride is formed as a byproduct during the production of perchloroethylene (PCE) and trichloroethylene (TCE). PCE and TCE are produced separately or as coproducts by either chlorination or oxychlorination of ethylene dichloride (EDC) or other C_2 chlorinated hydrocarbons. The relative proportions of the two products are determined by raw material ratios and reactor conditions.[40]

Process Descriptions

Ethylene Dichloride Chlorination Process --

The major products of the EDC chlorination process are TCE, PCE, and hydrogen chloride. Basic operations that may be used in EDC chlorination are shown in Figure 12.

Ethylene dichloride (Stream 1) and chlorine (Stream 2) are vaporized and fed to the reactor. Other chlorinated C_2 hydrocarbons or recycled chlorinated hydrocarbon byproducts may also be fed to the reactor. The chlorination is carried out at 400 to $450^{\circ}C$, slightly above atmospheric pressure. Hydrogen chloride byproduct (Stream 3) is separated from the chlorinated hydrocarbon mixture (Stream 4) produced in the reactor. The chlorinated hydrocarbon mixture (Stream 4) is neutralized with sodium hydroxide solution (Stream 5) and dried.[45]

The dried crude product (Stream 7) is separated by a distillation column into crude TCE (Stream 8) and crude PCE (Stream 9). The crude TCE (Stream 8) is fed to two columns in series which remove light ends (Stream 10) and heavy ends (Stream 13). TCE (Stream 12) is taken overhead from the heavy ends column and sent to TCE storage; the heavy ends (Stream 13) and the light ends (Stream 10) are combined, stored, and recycled.[45]

The crude PCE (Stream 9) from the PCE/TCE separation column is sent to the PCE column, where PCE (Stream 14) is removed as an overhead stream to PCE storage. Bottoms from this column (Stream 15) are sent to a heavy ends column and separated into heavy ends and tars. Heavy ends (Stream 16) are stored and recycled, and tars are incinerated.[45]

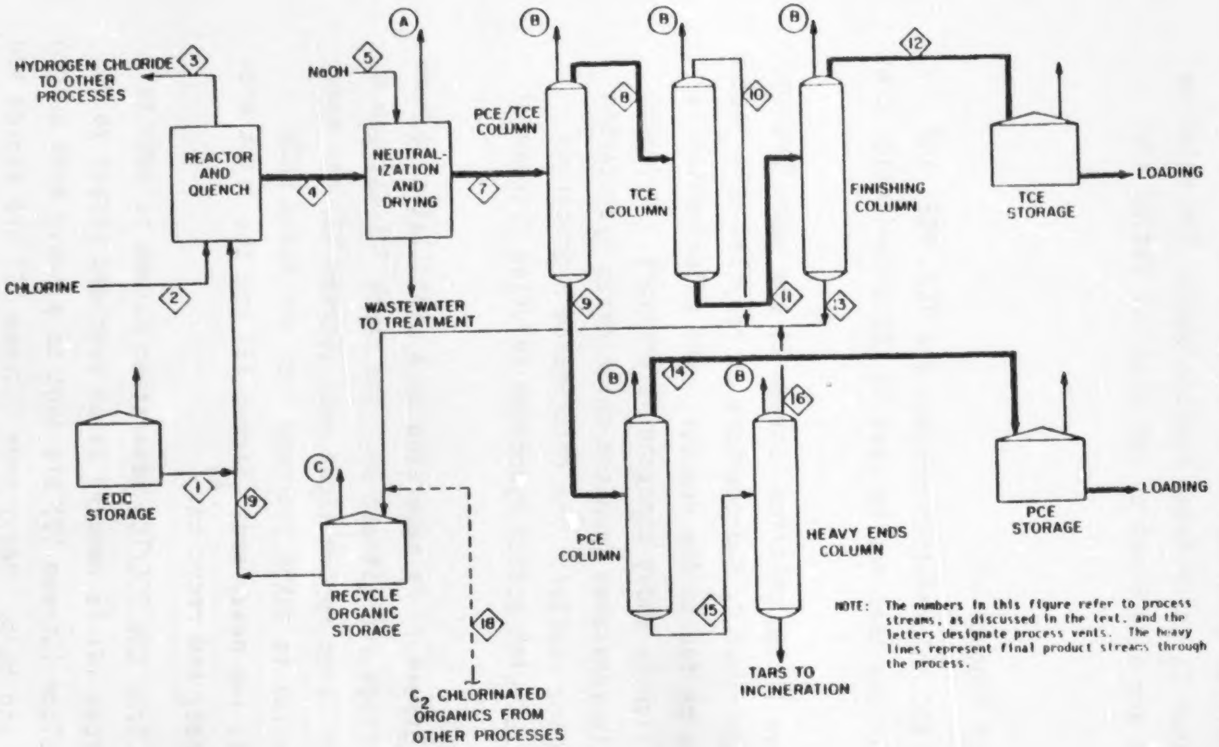

HYDROGEN CHLORIDE TO OTHER PROCESSES
3
REACTOR AND QUENCH
CHLORINE
2
NaOH
5
A
NEUTRAL-IZATION AND DRYING
4
7
WASTEWATER TO TREATMENT
PCE/TCE COLUMN
B
8
TCE COLUMN
10
9
11
FINISHING COLUMN
12
13
TCE STORAGE
LOADING
EDC STORAGE
1
19
C
RECYCLE ORGANIC STORAGE
18
C_2 CHLORINATED ORGANICS FROM OTHER PROCESSES
PCE COLUMN
14
15
HEAVY ENDS COLUMN
16
TARS TO INCINERATION
PCE STORAGE
LOADING
NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 12. Basic operations that may be used in perchloroethylene and trichloroethylene production by chlorination of ethylene dichloride.[45]

Ethylene Dichloride Oxychlorination Process --

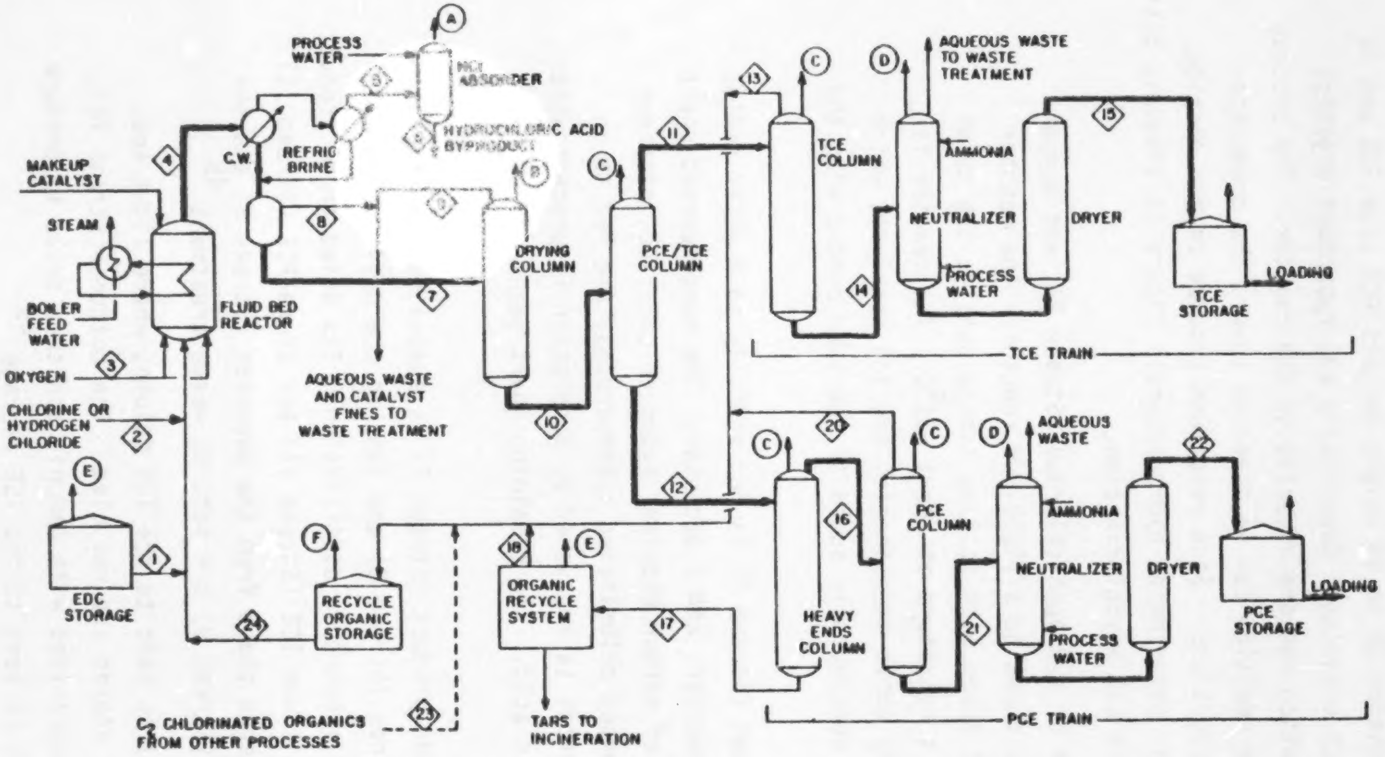
The major products of the EDC oxychlorination process are TCE, PCE, and water. The crude product contains 85 to 90 weight percent PCE plus TCE and 10 to 15 weight percent byproduct organics. Essentially all byproduct organics are recovered during purification and are recycled to the reactor. The process is very flexible, so that the reaction can be directed toward the production of PCE and TCE in varying proportions. Side reactions produce carbon dioxide, hydrogen chloride, and several chlorinated hydrocarbons. Figure 13 presents basic operations that may be used in EDC oxychlorination.

EDC (Stream 1), chlorine or hydrogen chloride (Stream 2), and oxygen (Stream 3) are fed in the gas phase to a fluid-bed reactor. The reactor contains a vertical bundle of tubes with boiling liquid outside the tubes which maintains the reaction temperature at about 425°C. The reactor is operated at pressures slightly above atmospheric, and the catalyst, which contains copper chloride, is continuously added to the tube bundle with the crude product.[45]

The reactor product stream (Stream 4) is fed serially to a water cooled condenser, a refrigerated condenser, and a decanter. The noncondensed inert gases (Stream 5), consisting of carbon dioxide, hydrogen chloride, nitrogen, and a small amount of uncondensed chlorinated hydrocarbons, are fed to an absorber, where hydrogen chloride is recovered by absorption in process water to make byproduct hydrochloric acid. The remaining inert gases are purged (Vent A).[45]

In the decanter, the crude product (Stream 7) is separated from the aqueous phase and catalyst fines (Stream 8) and sent to the drying column for removal of dissolved water by azeotropic distillation. The dried crude product (Stream 10) is separated into crude TCE (Stream 11) and crude PCE (Stream 12) in a PCE/TCE column. The aqueous phase from the decanter (Stream 8) and the water from the drying column (Stream 9) are sent to waste treatment.[45]

The crude TCE (Stream 11) is sent to the TCE column, where light ends (Stream 13) are removed to be stored and recycled. The bottoms (Stream 14), containing mainly TCE, are neutralized with ammonia and then dried to produce finished TCE (Stream 15) which is sent to the TCE storage.[45]


PROCESS WATER
HCl ABSORBER
HYDROCHLORIC ACID BYPRODUCT
MAKEUP CATALYST
STEAM
BOILER FEED WATER
FLUID BED REACTOR
C.W.
REFRIG BRINE
OXYGEN
CHLORINE OR HYDROGEN CHLORIDE
EDC STORAGE
DRYING COLUMN
PCE/TCE COLUMN
AQUEOUS WASTE AND CATALYST FINES TO WASTE TREATMENT
TCE COLUMN
NEUTRALIZER
AMMONIA
PROCESS WATER
DRYER
AQUEOUS WASTE TO WASTE TREATMENT
TCE STORAGE
LOADING
TCE TRAIN
RECYCLE ORGANIC STORAGE
ORGANIC RECYCLE SYSTEM
TARS TO INCINERATION
C_2 CHLORINATED ORGANICS FROM OTHER PROCESSES
HEAVY ENDS COLUMN
PCE COLUMN
AQUEOUS WASTE
PCE STORAGE
PCE TRAIN
A
B
C
D
E
F
1
2
3
4
5
6
7
8
9
10
11
12
13
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15
16
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24

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 13. Basic operations that may be used in perchloroethylene and trichloroethylene production by oxychlorination of ethylene dichloride.[45]

The crude PCE (Stream 12) from the PCE/TCE separation column is fed to a heavy ends removal column where PCE and lights (Stream 16) go overhead to a PCE finishing column and the heavies (Stream 17) remaining as the bottoms are sent to the organic recycle system. Here the organics that can be recycled (Stream 18) are separated from tars and sent to the recycle organic storage. The tars are incinerated. The PCE and light ends (Stream 16) from the heavy ends column are fed to a light ends removal column. Light ends (Stream 20) are removed overhead and are stored and recycled. The PCE bottoms (Stream 21) are neutralized with ammonia and then dried to obtain finished PCE (Stream 22) which is sent to the PCE storage.[45]

Emissions

Potential process sources of carbon tetrachloride emissions for the EDC chlorination process (Figure 12) are the neutralization and drying area vent (Vent A) and the distillation column vents (Vents B). Other carbon tetrachloride emission sources include the recycle organic storage tank (Vent C) and process fugitive emission sources.[45]

In the EDC oxychlorination process (Figure 13), potential process sources of carbon tetrachloride emissions are the hydrogen chloride absorber vent (Vent A), the drying column vent (Vent B), the distillation column vents (Vents C), the TCE and the PCE neutralizer vents (Vents D), and the organic recycle system vent (Vent E). Other carbon tetrachloride emission sources include the recycle organic storage tank (Vent F) and process fugitive emission sources.[45]

Table 17 presents uncontrolled carbon tetrachloride emission factors for a plant which produces perchloroethylene by the chlorination of ethylene dichloride. Also listed in this table are control techniques used at this facility and associated emission factors for controlled emissions. Emission factors for process and storage emissions were calculated from hourly carbon tetrachloride emission rates and a daily perchloroethylene production rate of 91 Mg reported by plant personnel,[46] assuming 24 hours per day operation. The carbon tetrachloride emission rate for fugitive sources was calculated from a VOC emission rate of 11 Mg per day[46] reported by the plant, assuming the fugitive emissions to be the same composition as total process emissions (0.61 percent).

TABLE 17. CONTROLLED AND UNCONTROLLED CARBON TETRACHLORIDE EMISSION FACTORS REPORTED BY A PLANT PRODUCING PERCHLOROETHYLENE BY ETHYLENE DICHLORIDE CHLORINATION[a]

Emission source	Uncontrolled carbon tetrachloride emission factor[b]	Control technique	% reduction[c]	Controlled carbon tetrachloride emission factor[b]
Process				
Neutralization	0.016 kg/Mg	None	--	--
Drying column	0.063 kg/Mg	Condenser	92	0.0050 kg/Mg
Distillation column	0.027 kg/Mg	None	--	--
Light ends/heavy ends mix tank	0.039 kg/Mg	Condenser	44	0.022 kg/Mg
Storage - light ends	0.11 kg/Mg	Condenser	99	0.0012 kg/Mg
Process fugitive[d]	2.8 kg/hr	None	--	--

[a] Any given perchloroethylene and/or trichoroethylene production plant may vary in configuration and level of control from this particular facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

[b] Emission factors in terms of kg/Mg refer to kilogram of carbon tetrachloride emitted per megagram of perchloroethylene produced.

[c] Emission reduction of control techniques reported by the plant.

[d] Fugitive emission rate independent of plant capacity.

It should be noted that carbon tetrachloride emissions may vary from plant to plant depending on the product mix produced. Thus, carbon tetrachloride emissions from other plants producing perchloroethylene and/or trichloroethylene may differ from those presented in Table 17.

Source Locations

Major producers of perchloroethylene and/or trichloroethylene for are presented in Table 18.

TABLE 18. FACILITIES PRODUCING PERCHLOROETHYLENE AND/OR TRICHLOROETHYLENE[15]

Company	Location	Chemical produced	
		PCE[a]	TCE[b]
Diamond Shamrock Corp.	Deer Park, TX	X	
Dow Chemical U.S.A.	Freeport, TX	X	X
	Pittsburg, CA	X	
	Plaquemine, LA	X	
I.E. duPont de Nemours and Co., Inc.	Corpus Christi, TX	X	
PPG Industries, Inc.	Lake Charles, LA	X	X
Stauffer Chemical Co.	Louisville, KY[c]	X	
Vulcan Materials Co.	Geismar, LA	X	
	Wichita, KS	X	

[a] PCE = perchloroethylene

[b] TCE = trichloroethylene

[c] Plant has been on standby since 1981.

Note: This is a list of major facilities producing perchloroethylene and/or trichloroethylene by any production process. Current information on which of these facilities produce these chemicals by ethylene dichloride chlorination or oxychlorination is not available. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves. The level of emissions from any given facility is a function of variables, such as throughput and control measures, and should be determined through direct contacts with plant personnel.

OTHER POTENTIAL SOURCES OF CARBON TETRACHLORIDE EMISSIONS

This section summarizes information on other potential sources of carbon tetrachloride air emissions. These source categories were identified using an emission inventory that reported carbon tetrachloride emissions for individual plants. It is not known whether these plants are representative of other facilities within the source category.

Chlorine Production

Chlorine is produced primarily by the electrolysis of aqueous brine solution. The electrolysis produces a stream of chlorine gas saturated with water vapor. This gas is cooled to condense out the water and is further dried by scrubbing with sulfuric acid. The resultant dry chlorine gas may be purified further by scrubbing with liquid chlorine. The purified chlorine is compressed and all or part of it may be further cooled by refrigeration to produce liquid chlorine.[47]

One company has developed a system using carbon tetrachloride as a recirculating solvent to recover chlorine from residual gases from the liquefaction process, handling, and storage.[48] The use of carbon tetrachloride as a scrubbing solution results in atmospheric emissions of carbon tetrachloride.[49]

Major producers of chlorine for which location and production data are available are presented in Table 19. It is not known whether these facilities use carbon tetrachloride.

Phosgene/Isocynate/Polyurethane Production

Phosgene is produced by reacting chlorine gas and carbon monoxide in the presence of activated carbon at 200°C. Hot reactor offgases are condensed to remove most of the phosgene and are then scrubbed with a hydrocarbon solvent to remove entrained phosgene.[50] Almost all of the phosgene produced domestically is used directly in other operations in the same plant. The principal use is in the manufacture of isocyanates which are used in making polyurethane resins.[51]

One toluene diisocyanate plant reported carbon tetrachloride emissions in 1980.[49] This may be due to carbon tetrachloride scrubbing of a phosgene process stream, which would be considered part of the isocyanate process.

TABLE 19. CHLORINE PRODUCTION FACILITIES[15]

Company	Location
Aluminum Co. of America	Point Comfort, TX
AMAX Inc.	
AMAX Specialty Metals Corp., subsid.	Rowley, UT
BASF Wyandotte Corp.	
Indust. Chems. Group	
Basic Chems. Div.	Geismar, LA
Brunswick Pulp & Paper Co.	
Brunswick Chem. Co., div.	Brunswick, GA
Champion Internat'l Corp.	
Champion Papers Div. - Chems. & Associated Products	Canton, NC
Diamond Shamrock Corp.	
Indust. Chems. and Plastics Unit	
Electro Chems. Div.	Deer Park, TX
	Delaware City, DE
	La Porte, TX
	Mobile, AL
	Muscle Shoals, AL
Dow Chem. U.S.A.	Freeport, TX
	Midland, MI
	Oyster Creek, TX
	Pittsburg, CA
	Plaquemine, LA
E.I. duPont de Nemours & Co., Inc.	
Chems. and Pigments Dept.	Niagara Falls, NY
Petrochems. Dept.	
Freon® Products Div.	Corpus Christi, TX
Ethyl Corp.	
Chems. Group	Baton Rouge, LA
FMC Corp.	
Indust. Chem. Group	South Charleston, WV
Formosa Plastics Corp. U.S.A.	Baton Rouge, LA
Fort Howard Paper Co.	Green Bay, WI
	Muskogee, OK
Gen. Electric Co.	
Engineered Materials Group	
Plastics Business Operations	Mount Vernon, IN
Georgia-Pacific Corp.	
Chem. Div.	Bellingham, WA
	Plaquemine, LA
The BF Goodrich Co.	
Convent Chem. Corp., sudsid.	Calvert City, KY
	Convent, LA
Hercules Inc.	Hopewell, VA

CONTINUED

TABLE 19. (continued)

Company	Location
Kaiser Aluminum & Chem. Corp.	
Kaiser Indust. Chems. Div.	Gramercy, LA
Linden Chems. & Plastics, Inc.	
LCP Chems. Divisions	Acme, NC
	Ashtabula, OH
	Brunswick, GA
	Linden, NJ
	Moundsville, WV
	*Niagara Falls, NY
	Orrington, ME
	Syracuse, NY
Mobay Chem. Corp.	
Inorganic Chems. Div.	Cedar Bayou, TX
Monsanto Co.	
Monsanto Chem. Intermediates Co.	Sauget, IL
Occidental Petroleum Corp.	
Hooker Chem. Corp., subsid.	
Indust. Chems. Group	Hahnville, LA
	Montague, MI
	Niagrara Falls, NY
	Tacoma, WA
Olin Corp.	
Olin Chems. Group	Augusta, GA
	Charleston, TN
	McIntosh, AL
	Niagara Falls, NY
Oregon Metallurgical Corp.	Albany, OR
Pennwalt Corp.	
Chems. Corp.	
Inorganic Chem. Div.	Portland, OR
	Tacoma, WA
	Wyandotte, MI
PPG Indust., Inc.	
Indust. Chem. Div.	Barberton, OH
	Lake Charles, LA
	Natrium, WV
RMI Co.	Ashtabula, OH
Shell Chem. Co.	Deer Park, TX
Stauffer Chem. Co.	
Indust. Chem. Div.	Henderson, NV
	LeMoyne, AL
	St. Gabriel, LA
Titanium Metals Corp. of America	
TIMET Div.	Henderson, NV
Vertac Chem. Corp.	Vicksburg, MS

CONTINUED

TABLE 19. (continued)

Vulcan Materials Co.	
Vulcan Chems., Div.	Denver City, TX
	Geismar, LA
	Port Edwards, WI
	Wichita, KS
Weyerhaeuser Co.	Longview, WA

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*Joint venture with Occidental Petroleum Corporation, Occidental Chemical Corporation, subsidiary.

NOTE: Information is not available to determine which of these facilities use carbon tetrachloride. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current listings or the plants themselves.

Major producers of phosgene for which location and production data are available are listed in Table 20. It is not known whether these facilities use carbon tetrachloride.

Pesticide Production

Emissions of carbon tetrachloride were reported to be associated with several pesticide production operations.[49] Carbon tetrachloride is used as a solvent or reaction medium in these processes. Carbon tetrachloride may be used as a solvent in other pesticide production processes; however, data are not available to estimate total carbon tetrachloride usage in pesticide manufacture. The Standard Industrial Classification code for agricultural chemical manufacturing is 287.

Miscellaneous Industrial Solvent Usage

As noted in previous subsections, carbon tetrachloride is used as a solvent in the manufacture of pharmaceuticals and pesticides. Carbon tetrachloride is also used as a solvent in the manufacture of other specialty and small-volume chemicals. Carbon tetrachloride emissions have been reported for the production of Hypalon®, a synthetic rubber, for resinous chlorowax production, and for the production of tetrachloropyridene and 4-amino-3,5,7-trichloropicolinic acid.[49] Data are not available to estimate total carbon tetrachloride solvent use in chemical manufacture or to identify all industries where carbon tetrachloride is used.

Treatment, Storage and Disposal Facilities

Considerable potential exists for volatile substances, including carbon tetrachloride, to be emitted from hazardous waste treatment, storage and handling facilities. A California study[52] shows that significant levels of carbon tetrachloride may be contained in hazardous wastes shipped to various kinds of disposal facilities. Volatilization of carbon tetrachloride and other substances was confirmed in this study by significant ambient air concentrations over one site. Reference 53 provides general theoretical models for estimating volatile substance emissions from a number of generic kinds of waste handling operations, including surface impoundments, landfills, landfarming (land treatment) operations, wastewater treatment systems, and

TABLE 20. PHOSGENE PRODUCTION FACILITIES[15]

Company	Location
BASF Wyandotte Corp. Polymers Group Urethanes Chems. Business	Geismar, LA
Dow Chem. U.S.A.	Freeport, TX
E.I. duPont de Nemours & Co., Inc. Polymer Products Dept.	Deepwater, NJ
Essex Chem. Corp. Minerec Corp., subsid.	Baltimore, MD
Gen. Electric Co. Engineered Materials Group Plastics Business Operations	Mount Vernon, IN
ICI Americas Inc. Rubicon Chems. Inc., subsid.	Geismar, LA
Mobay Chem. Corp. Polyurethane Div.	Cedar Bayou, TX New Martinsville, WV
Olin Corp. Olin Chems. Group	Lake Charles, LA Moundsville, WV
PPG Indust., Inc. Agricultural and Performance Chems. Div. Specialty Products Unit	Barberton, OH La Porte, TX[a]
Union Carbide Corp. Agricultural Products Group	Institute, WV
The Upjohn Co. Polymer Chems. Div.	La Porte, TX
Van De Mark Chem. Co., Inc.	Lockport, NY[a]

[a] These two plants are believed to be the only ones producing phosgene for sale; all others produce phosgene for captive consumption.

Note: Information is not available to determine which of these facilities use carbon tetrachloride. This list is subject to change as market conditions change, facility ownership changes, or plants are closed down. The reader should verify the existence of particular facilities by consulting current lists or the plants themselves.

drum storage/handling processes. If such a facility is known to handle carbon tetrachloride, the potential should be considered for some air emissions to occur.

Several studies show that carbon tetrachloride may be emitted from municipal wastewater treatment plants, albeit at quite low levels. In a bench scale test, the potential was demonstrated for carbon tetrachloride volatilization from clarifiers and aeration basins.[54] However, actual tests at one municipal treatment plant (handling about 50% industrial sewage) showed carbon tetrachloride emissions to be consistently below 184 grams (0.4 pounds) per day, assuming all carbon tetrachloride in the influent is air stripped during treatment.[55] Furthermore, tests at a smaller treatment facility (handling about 40% industrial and 60% municipal sewage) showed carbon tetrachloride emission levels to be virtually undetectable.[56]

SECTION 5

SOURCE TEST PROCEDURES

Carbon tetrachloride emissions can be measured using EPA Reference Method 23, which was proposed in the Federal Register on June 11, 1980.[57] EPA has validated Method 23 in the laboratory for carbon tetrachloride[58] but has not validated the method for carbon tetrachloride in the field.[59]

In Method 23, a sample of the exhaust gas to be analyzed is drawn into a Tedlar® or aluminized Mylar® bag as shown in Figure 15. The bag is placed inside a rigid leak proof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. Sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography (GC) coupled with flame ionization detection (FID). Analysis should be conducted within 1 day of sample collection. The recommended GC column is 3.05 m by 3.2 mm stainless steel, filled with 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. This column normally provides an adequate resolution of halogenated organics. (Where resolution interferences are encountered, the GC operator should select the column best suited to the analysis.) The column temperature should be set at 100°C. Zero helium or nitrogen should be used as the carrier gas at a flow rate of approximately 20 ml/min.

The peak area corresponding to the retention time of carbon tetrachloride is measured and compared to peak areas for a set of standard gas mixtures to determine the carbon tetrachloride concentration. The range of the method is 0.1 to 200 ppm; however, the upper limit can be extended by extending the calibration range or diluting the sample. The method does not apply when carbon tetrachloride is contained in particulate matter.

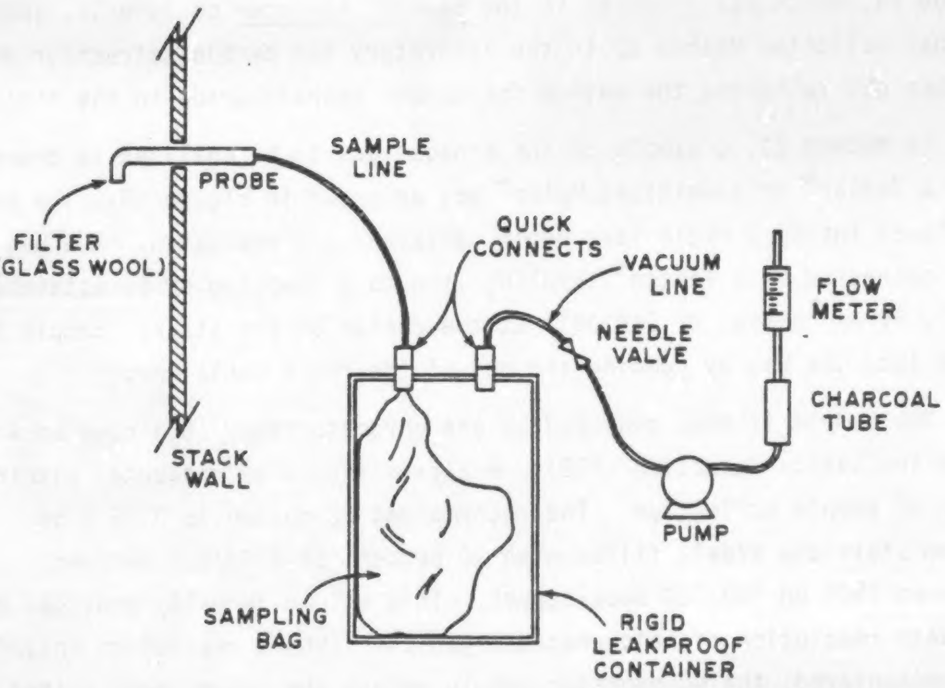
SAMPLE LINE
PROBE
FILTER (GLASS WOOL)
QUICK CONNECTS
VACUUM LINE
FLOW METER
NEEDLE VALVE
CHARCOAL TUBE
STACK WALL
PUMP
SAMPLING BAG
RIGID LEAKPROOF CONTAINER

Figure 15. Method 23 sampling train.[57]

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APPENDIX

EMISSION FACTORS FOR CARBON TETRACHLORIDE PRODUCTION

This appendix presents the derivations of carbon tetrachloride emission factors for carbon tetrachloride production processes that are presented in Tables 2 through 6. Emission factors for the hydrocarbon chlorinolysis (perchloroethylene coproduct) process (Table 2) were developed based on a hypothetical plant with a total production capacity of 80,000 Mg and a product mix of 37.5 percent carbon tetrachloride and 62.5 percent perchloroethylene.[1] Emission factors for the methane chlorination process (Table 3) are based on a hypothetical plant with a total chloromethane production capacity of 200,000 Mg, and a product mix of 20 percent methyl chloride, 45 percent methylene chloride, 25 percent chloroform, and 10 percent carbon tetrachloride.[2] Emission factors for the carbon disulfide chlorination process (Table 4) were developed based on operating data on the Stauffer plant in Lemoyne, Alabama,[3,4] the only plant currently using this production process. Emission factors for the methanol hydrochlorination/methyl chloride chlorination process were developed based on a hypothetical plant with a total chloromethane production capacity of 90,000 Mg/yr and a product mix of 25 percent methyl chloride, 48 percent methylene chloride, 25 percent chloroform, and 2 percent byproduct carbon tetrachloride.[5]

The following sections describe the derivations of carbon tetrachloride emission factors for process vent emissions; in-process and product storage tank emissions; secondary emissions from liquid, solid, and aqueous waste streams; handling emissions from loading product carbon tetrachloride; and fugitive emissions from leaks in process valves, pumps, compressors, and pressure relief valves.

PROCESS EMISSION FACTORS

Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct)

Carbon tetrachloride process emissions from chlorinolysis process result from the purging of inert gases from the carbon tetrachloride distillation condenser (Vent A, Figure 2). The uncontrolled emission factor for emissions from the distillation column was derived from the annual carbon tetrachloride emission rate of 180 kg and associated carbon tetrachloride thruput of 15×10^6 liters reported by one facility[6] and the density of carbon tetrachloride (1.59 g/ml):

$$\text{Emission factor} = \frac{180 \text{ kg}}{15 \times 10^6 \ \ell \times 1.59 \text{ g}/10^{-3}\ell}$$

$$= \frac{180 \text{ kg}}{2.4 \times 10^4 \text{ Mg}}$$

$$= 0.008 \text{ kg/Mg}$$

Another potential source of process emissions is the caustic scrubber vent (Vent E, Figure 2); however, no emissions have been reported for this source.[1]

Methane Chlorination

Carbon tetrachloride process emissions from the methane chlorination process result from venting of the inert gases from the recycle methane stream (Vent A, Figure 3) and from emergency venting of the distillation area inert gases (Vent C, Figure 3).

Recycled Methane Inert Gas Purge vent--

The uncontrolled emission factor for the recycled methane inert gas purge vent was calculated from a carbon tetrachloride emission factor of 4.2×10^{-3} kg per Mg total chloromethane production capacity and the representative plant's carbon tetrachloride production of 10 percent of total chloromethane production. This emission factor represents an upper bound estimate.[2]

$$\text{Emission factor} = 4.2 \times 10^{-3} \ \frac{\text{kg } CCl_4}{\text{Mg total prod.}} \times \frac{\text{total prod.}}{0.10 \ CCl_4 \text{ prod.}}$$

$$= 0.042 \text{ kg/Mg}$$

Distillation Area Emergency Inert Gas Vent--

The uncontrolled emission factor for the distillation area emergency inert gas vent was derived from an emission factor for volatile organic compounds (VOC) of 0.20 kg/Mg total chloromethane production capacity[2] and composition data showing carbon tetrachloride to be 2.6 percent of VOC.[7] No information was available on the assumptions upon which the derivation of this VOC emission factor were based. The calculation of carbon tetrachloride emissions per unit carbon tetrachloride produced was made using a carbon tetrachloride production rate of 10 percent of total chloromethanes production.

$$\text{Emission factor} = 0.20\ \frac{\text{kg VOC}}{\text{Mg total prod}} \times \frac{0.026\ \text{CCl}_4}{\text{VOC}} \times \frac{\text{total prod.}}{0.10\ \text{CCl}_4\ \text{prod}}$$

$$= 0.052\ \text{kg/Mg}$$

Carbon Disulfide Chlorination

The main source of carbon tetrachloride process emissions from the carbon disulfide chlorination process is the chlorination reactor which, at the Stauffer facility, is controlled with a two-stage refrigerated condenser (Vent A, Figure 4). The controlled emission factor for this source was calculated from a carbon tetrachloride hourly emission rate of 54 kg/hr determined from a source test and the plant's annual carbon tetrachloride production of 82,000 Mg/yr,[4] assuming 8,760 hours per year operation.

$$\begin{array}{l}\text{Emission factor}\\ \text{(controlled)}\end{array} = \frac{54\ \text{kg/hr} \times 8{,}760\ \text{hr/yr}}{82{,}000\ \text{Mg/yr}}$$

$$= 5.8\ \text{kg/Mg}$$

The uncontrolled emission factor was calculated from the controlled emission factor and the reproted control efficiency of 95 percent for the condenser.[8]

$$\begin{array}{l}\text{Emission factor}\\ \text{(uncontrolled)}\end{array} = \frac{5.8\ \text{kg/Mg}}{1 - 0.95}$$

$$= 116\ \text{kg/Mg}$$

Methanol Hydrochlorination/Methyl Chloride Chlorination

Process vents are not a significant source of carbon tetrachloride emissions in this process.[5]

STORAGE EMISSION FACTORS

In calculating storage emission factors, all storage tanks were assumed to be fixed roof tanks.[1,2,5] Uncontrolled carbon tetrachloride emission factors for in-process and product storage for the hydrocarbon chlorinolysis process (Vents B, C, and D, Figure 2), methane chlorination process (Vents B, D, and E, Figure 3), the carbon disulfide chlorination process (Vent B, Figure 4), and methanol hydrochlorination process (Vents A, B, and C, Figure 5) were calculated using emission equations for breathing and working losses for fixed roof tanks from reference 9:

$$L_T = L_B + L_W$$

$$L_B = 1.02 \times 10^{-5} M_v \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$$

$$L_W = 1.09 \times 10^{-8} M_v P V N K_n K_c$$

where,

L_T = total loss (Mg/yr)

L_B = breathing loss (Mg/yr)

L_W = working loss (Mg/yr)

M_v = molecular weight of product vapor (lb/lb mole)

P = true vapor pressure of product (psia)

D = tank diameter (ft)

H = average vapor space height (ft): use tank specific values or an assumed value of one-half the tank height

T = average diurnal temperature change in °F

F_p = paint factor (dimensionless); assume a value of 1 for a white tank in good condition

C = tank diameter factor (dimensionless):

for diameter $\geq$ 30 feet, $C = 1$

for diameter < 30 feet,

$$C = 0.0771\ D - 0.0013(D^2) - 0.1334$$

K_c = product factor (dimensionless) = 1.0 for VOL:

V = tank capacity (gal)

N = number of turnovers per year (dimensionless)

K_n = turnover factor (dimensionless):

for turnovers > 36, $K_n = \frac{180 + N}{6N}$

for turnovers $\leq$ 36, $K_n = 1$

For the hydrocarbon chlorinolysis, methane chlorination and methanol hydrochlorination/methyl chloride chlorination processes, hypothetical plant storage tank conditions from references 1, 2, and 5, respectively, were used for the calculations. The tank conditions given by these references include tank volume, number of turnovers per year, bulk liquid temperature, and an assumed diurnal temperature variation of 20°C. The diameters (D), in feet, of the tanks were calculated from given tank volumes (V), in gallons, with heights (h), in feet, assumed at 8 foot intervals,[10] from:

$$D = 2\sqrt{\frac{V/7.481}{\pi \times h}}$$

For tanks containing mixtures, the vapor pressure of the mixture in the tank, molecular weight of vapor, and weight percent of carbon tetrachloride in the vapor were calculated. The calculations of emission factors for all production processes are summarized in Table A-1. Sample calculations are presented in their entirety for the hydrocarbon chlorinolysis process. For the other three processes, storage tank parameters and vapor composition data used in the calculations of the emission factors listed in Table A-1 are presented in tables.

Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct)

Emission factors for the crude product tank, two carbon tetrachloride day storage tanks, and the carbon tetrachloride product tank were calculated using the tank parameters listed in Table A-2.

Crude Product Tank--

Composition -- The composition of the mixture in the crude product tank is based on the hypothetical plant mixture. The mole fractions of the liquid components were derived from these weight fractions and molecular weights. The mole fractions of the components in liquid were then multiplied by

TABLE A-1. SUMMARY OF CALCULATIONS OF CARBON TETRACHLORIDE STORAGE EMISSION FACTORS

PROCESS Tank	Breathing Loss, L_B (Mg/yr)	Working Loss, L_W (Mg/yr)	Total Loss, L_T (Mg/yr)	Percent Carbon Tetrachloride In Vapor	Number of Tanks	Carbon Tetrachloride Production (Mg/yr)	Emission Factor (kg/Mg)
HYDROCARBON CHLORINOLYSIS							
Crude	1.86	2.00	3.86	76	1	30,000	0.098
Day	0.75	5.92	6.67	100	2	30,000	0.45
Product	2.92	14.5	17.4	100	1	30,000	0.58
METHANE CHLORINATION							
Crude	10.4	11.5	21.9	5.2	1	20,000	0.057
Day	0.26	3.33	3.59	100	2	20,000	0.36
Product	2.92	9.87	12.8	100	1	20,000	0.64
METHYL CHLORIDE CHLORINATION							
Crude	3.62	2.97	6.59	1.1	1	1,800	0.040
Surge	1.21	1.08	2.29	4.5	1	1,800	0.057
Carbon Tetrachloride	0.30	2.20	2.50	100	1	1,800	1.4
CARBON DISULFIDE CHLORINATION							
Small	3.84	6.68	10.5	100	2	81,600	0.26
Large	6.93	13.4	20.3	100	2	81,600	0.50

TABLE A-2. STORAGE TANK PARAMETERS FOR HYDROCARBON CHLORINOLYSIS (PERCHLOROETHYLENE COPRODUCT) PROCESS.

Tanks	Crude	Day	Product
Number of tanks	1	2	1
Volume (V), gal	100,000	20,000	200,000
Height (h), ft	32	16	40
Vapor space height (H), ft	16	8	20
Diameter (D), ft	23	15	29
Turnovers/yr (N)	6	125	25
Temperature, °F	100	95	68
Vapor pressure (P), psia	1.95	3.44	1.73
Diurnal temperature change (T), °F	22	22	22
Molecular weight of vapor (M_v), lb/lb mole	157	154	154
Turnover factor (K_n)	1	0.41	1
Tank diameter factor (C)	0.95	0.73	1.0

the vapor pressures of each component to determine component partial pressures, the sum of which is the total vapor pressure, P. Mole fractions of the components in the vapor phase were calculated as the ratio of component partial pressures to total vapor pressure. The molecular weight of the vapor mixture (M_v) was calculated as the sum of the products of the component partial pressures and their molecular weights, ignoring the molecular weight of the air. The weight percent of components in vapor were calculated from the ratios of the product of the mole fraction in vapor and molecular weight to the molecular weight of the vapor mixture. These calculations are summarized in Table A-3.

Tank emissions-- With the parameters listed in Table A-2, total tank losses were calculated as follows:

$$L_B = (1.02 \times 10^{-5})(157)\left(\frac{1.95}{14.7-1.95}\right)^{0.68}(23)^{1.73}(16)^{0.51}(22)^{0.5}(1)(0.95)(1)$$
$$= (1.02 \times 10^{-5})(157)(0.28)(227)(4.11)(4.69)(0.95)$$
$$= 1.86 \text{ Mg/yr}$$

$$L_W = (1.09 \times 10^{-8})(157)(1.95)(100,000)(6)(1)(1)$$
$$= 2.00 \text{ Mg/yr}$$

$$L_T = L_B + L_W = 3.86 \text{ Mg/yr}$$

Emission factor-- The carbon tetrachloride emission factor was calculated from total annual tank loss, fraction of vapor mixture that is carbon tetrachloride, and the representative plant production rate of 30,000 Mg/yr:

$$\text{Emission factor} = \frac{(3.86 \text{ Mg/yr})(0.76)}{30,000 \text{ Mg/yr}}$$
$$= 0.098 \text{ kg/Mg}$$

Day Tanks--

Tank emissions--

$$L_B = (1.02 \times 10^{-5})(154)\left(\frac{3.44}{14.7-3.44}\right)^{0.68}(15)^{1.73}(8)^{0.51}(22)^{0.5}(1)(0.73)(1)$$
$$= (1.02 \times 10^{-5})(154)(0.45)(108)(2.89)(4.69)(0.73)$$
$$= 0.75 \text{ Mg/yr}$$

$$L_W = (1.09 \times 10^{-8})(154)(3.44)(20,000)(125)(0.41)(1)$$
$$= 5.92 \text{ Mg/yr}$$

$$L_T = L_B + L_W = 6.67 \text{ Mg/yr}$$

TABLE A-3. SUMMARY OF COMPOSITION CALCULATIONS FOR HYDROCARBON CHLORINOLYSIS (PERCHLOROETHYLENE COPRODUCT) - CRUDE PRODUCT STORAGE TANK

LIQUID COMPOSITION:

Component	Weight percent in liquid, w_l	Molecular weight, MW	Moles in liquid, m_l (w_l/MW)	Mole fraction in liquid, x_l (m_l/M_l)
Carbon tetrachloride	37.5	154	0.24	0.39
Perchloro-ethylene	62.5	166	0.38 M_l = 0.62	0.61

VAPOR COMPOSITION:

Component	Vapor pressure (psia), P^o	Partial pressure, P_p $(P^o \times x_l)$	Mole fraction in vapor, x_v (P_p/P)	Weight in vapor, g_v $(x_v \times MW)$	Weight percent in vapor $([g_v/M_v] \times 100)$
Carbon tetrachloride	3.9	1.52	0.78	120	76
Perchloro-ethylene	0.71	0.43 P= 1.95	0.22	37 M_v = 157	24

Emission factor --

$$\text{Emission factor} = \frac{6.67\ \frac{\text{Mg/yr}}{\text{tank}} \times 2\ \text{tanks}}{30{,}000\ \text{Mg/yr}}$$

$$= 0.45\ \text{kg/Mg}$$

Product tank--

Tank emissions--

$$L_B = (1.02 \times 10^{-5})(154)\left(\frac{1.73}{14.7-1.73}\right)^{0.68}(29)^{1.73}(20)^{0.51}(22)^{0.5}(1)(1)(1)$$

$$= (1.02 \times 10^{-5})(154)(0.254)(339)(4.6)(4.69)$$

$$= 2.92\ \text{Mg/yr}$$

$$L_W = (1.09 \times 10^{-8})(154)(1.73)(200{,}000)(25)$$

$$= 14.5\ \text{Mg/yr}$$

$$L_T = L_B + L_W = 17.4\ \text{Mg/yr}$$

Emission factor

$$\text{Emission factor} = \frac{17.4\ \text{Mg/yr}}{30{,}000\ \text{Mg/yr}}$$

$$= 0.58\ \text{kg/Mg}$$

Methane Chlorination

Emission factors for the crude product tank, two carbon tetrachloride day tanks, and the carbon tetrachloride product tank were calculated using the tank parameters listed in Table A-4. The calculations of the composition of the vapor for the crude product tank are summarized in Table A-5.

Methanol Hydrochlorination/Methyl Chloride Chlorination

Emission factors for the crude product tank, the surge tank, and the carbon tetrachloride tank were calculated using the tank parameters listed in Table A-6. The calculations of the compositions of the vapor for the crude product tank and the surge tank are presented in Tables A-7 and A-8, respectively.

Carbon Disulfide Chlorination

Emission factors for two small carbon tetrachloride tanks and two large tanks were calculated from reported tank parameters for the Stauffer facility.[3] These parameters and assumed values are summarized in Table A-9.

TABLE A-4. STORAGE TANK PARAMETERS FOR METHANE CHLORINATION PROCESS

Tank	Crude	Day	Product
Number of tanks	1	2	1
Volume (V), gal	200,000	10,000	200,000
Height (h), ft	40	16	40
Vapor space height (H), ft	20	8	20
Diameter (D), ft	29	10	29
Turnovers/yr (N)	6	166	17
Temperature, °F	95	95	68
Vapor pressure (P), psia	9.50	3.44	1.73
Diurnal temperature change (T), °F	22	22	22
Molecular weight of vapor (M_v), lb/lb mole	93	154	154
Turnover factor (K_n)	1	0.347	1
Tank diameter factor (C)	1	0.508	1

TARLE A-5. SUMMARY OF COMPOSITION CALCULATIONS FOR METHANE CHLORINATION - CRUDE PRODUCT TANK

LIQUID COMPOSITION:

Component	Weight percent in liquid, w_l	Molecular weight, MW	Moles in liquid, m_l (w_l/MW)	Mole fraction in liquid, x_l (m_l/M_l)
Methylene chloride	56	85	0.66	0.66
Chloroform	31	119	0.26	0.26
Carbon tetrachloride	13	154	0.084	0.084
			M_l= 1.00	

VAPOR COMPOSITION:

Component	Vapor pressure (psia), P^o	Partial pressure, P_p ($P^o \times x_l$)	Mole fraction in vapor, x_v (P_p/P)	Weight in vapor, g_v (x_v x MW)	Weight percent in vapor ($[g_v/M_v]$ x 100)
Methylene chloride	11.6	7.66	0.81	69	0.74
Chloroform	5.96	1.55	0.16	19	0.20
Carbon tetrachloride	3.44	0.29	0.031	4.8	0.052
		P= 9.50		M_v= 92.8	

TABLE A-6. STORAGE TANK PARAMETERS FOR METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION PROCESS

Tanks	Crude	Surge	Carbon Tetrachloride
Number of tanks	1	1	1
Volume (V), gal	50,000	20,000	10,000
Height (h), ft	24	16	16
Vapor space height (H), ft	12	8	8
Diameter (D), ft	19	15	10
Turnovers/yr (N)	6	6	32
Temperature, °F	95	104	104
Vapor pressure (P), psia	10	6.9	4.1
Diurnal temperature change (T), °F	22	22	22
Molecular weight of vapor (M_v), lb/lb mole	91	120	154
Turnover factor (K_n)	1	1	1
Tank diameter factor (C)	0.862	0.731	0.508

TABLE A-7. SUMMARY OF COMPOSITION CALCULATIONS FOR METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION - CRUDE PRODUCT TANK

LIQUID COMPOSITION:

Component	Weight percent in liquid, w_l	Molecular weight, MW	Moles in liquid, m_l (w_l/MW)	Mole fraction in liquid, x_l (m_l/M_l)
Methylene chloride	64	85	0.753	0.72
Chloroform	33	119	0.277	0.26
Carbon tetrachloride	3	154	0.019 $M_l =$ 1.049	0.018

VAPOR COMPOSITION:

Component	Vapor pressure (psia), P^o	Partial pressure, P_p $(P^o \times x_l)$	Mole fraction in vapor, x_v (P_p/P)	Weight in vapor, g_v $(x_v \times MW)$	Weight percent in vapor $([g_v/M_v] \times 100)$
Methylene chloride	11.6	8.35	0.84	71	78
Chloroform	5.96	1.55	0.16	19	21
Carbon tetrachloride	3.44	0.062 $P =$ 9.962	0.0062	0.96 $M_v =$ 90.96	1.1

TABLE A-8. SUMMARY OF COMPOSITION CALCULATIONS FOR METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION - SURGE TANK

LIQUID COMPOSITION:

Component	Weight percent in liquid, w_l	Molecular weight, MW	Moles in liquid, m_l $(w_l/MW)^l$	Mole fraction in liquid, x_l $(m_l/M_l)^l$
Chloroform	92.6	119	0.778	0.94
Carbon tetrachloride	7.4	154	0.048 M_l = 0.826	0.058

VAPOR COMPOSITION:

Component	Vapor pressure (psia), P^o	Partial pressure, P_p $(P^o x\ x_l)^P$	Mole fraction in vapor, x_v $(P_p/P)^v$	Weight in vapor, g_v $(x_v$ x $MW)^v$	Weight percent in vapor ($[g_v/M_v]$ x 100)
Chloroform	7.09	6.66	0.97	115	96
Carbon tetrachloride	4.08	0.24 6.90	0.035	5.4 120.4	4.5

TABLE A-9. STORAGE TANK PARAMETERS FOR CARBON DISULFIDE CHLORINATION PROCESS

Tanks	Small	Large
Number of tanks	2	2
Volume (V), gal	230,000	460,000
Height (h), ft	29	29
Vapor space height (H), ft	15	15
Diameter (D), ft	37	52
Turnovers/yr (N)[a]	10	10
Temperature, °F[b]	68	68
Vapor pressure (P), psia	1.73	1.73
Diurnal temperature change (T), °F[b]	22	22
Molecular weight of vapor (M_v), lb/lb mole	154	154
Turnover factor (K_n)	1	1
Tank diameter factor (C)	1	1

[a] Tank throughput was estimated by assuming reported production (1.36×10^7 gal/yr) to be apportioned among the tanks according to size. Turnover rate was then calculated:

$$\text{turnover rate} = \frac{\text{thruput}}{\text{tank volume}}$$

[b] Assumed value.

SECONDARY EMISSIONS

Hydrocarbon Chlorinolysis (Perchloroethylene Coproduct)

Secondary emissions of carbon tetrachloride can result from the handling and disposal of process waste liquids. Two sources of secondary emissions from the hydrocarbon chlorinolysis process are the bottoms from the perchloroethylene distillation column (Source F, Figure 2), commonly called hex wastes, and the waste caustic from the caustic rubber (Source G, Figure 2). It should be noted that, lacking other data, emission factors for both sources were developed based on data from a plant which uses operating conditions that are much less severe than the chlorinolysis process.

Hex Wastes--

The uncontrolled emission factor for the combined sources of hex waste handling and waste hydrocarbon storage emissions was derived from a published VOC emission factor of 0.056 kg/Mg of total production capacity, composition data showing carbon tetrachloride to be 3.1 percent of VOC,[1] and the hypothetical plant carbon tetrachloride production of 37.5 percent total production:

$$\text{Emission factor} = \frac{0.056 \text{ kg VOC}}{\text{Mg total prod.}} \times \frac{0.031 \text{ CCl}_4}{\text{VOC}} \times \frac{\text{total prod.}}{0.375 \text{ CCl}_4 \text{ prod.}}$$

$$= 0.0046 \text{ kg/Mg}$$

Waste Caustic Handling--

The uncontrolled emission factor for secondary emissions from waste caustic handling is based on a plant's estimate of total VOC emissions per production capacity for waste caustic handling and disposal of 0.0011 kg VOC/Mg total production,[1] assuming that carbon tetrachloride is the main component of the VOC, and using the hppothetical plant's carbon tetrachloride production rate of 37.5 percent of total production:

$$\text{Emission factor} = \frac{0.0011 \text{ kg}}{\text{Mg total prod.}} \times \frac{\text{total prod.}}{0.375 \text{ CCl}_4 \text{ prod.}}$$

$$= 0.0029 \text{ kg/Mg}$$

Methane Chlorination

Secondary emissions of carbon tetrachloride from the methane chlorination process can result from the handling and disposal of process waste liquids. These liquid streams are indicated on the process flow diagram (Source F, Figure 3) and include waste caustic from the methyl chloride and methane recycle stream scrubbers, waste caustic from the crude chloromethane neutralizer, and salt solution from the crude chloromethanes dryer. The uncontrolled emission factor for these secondary carbon tetrachloride emissions was calculated using a carbon tetrachloride content of 10 parts per million reported for total wastewater discharges averaging 68 liters per minute,[7] the assumption that 100 percent of the carbon tetrachloride will be vaporized during on-site wastewater treatment, and the hypothetical plant carbon tetrachloride production of 20,000 Mg/yr:

$$\text{Emissions} = \frac{68\ \ell\ \text{water}}{\text{min}} \times \frac{1\ \text{kg}}{\ell\ \text{water}} \times \frac{10\ \text{kg CCl}}{10^6\ \text{kg water}} \times \frac{5.26 \times 10^5\ \text{min}}{\text{yr}}$$

$$\text{Emission factor} = \frac{357\ \text{kg/yr}}{20{,}000\ \text{Mg/yr}}$$

$$= 0.018\ \text{kg/Mg}$$

Carbon Disulfide Chlorination

Insufficient data are available to calculate an emission factor for secondary emissions of carbon tetrachloride from this process.

Methanol Hydrochlorination/methyl Chloride Chlorination

Potential sources of secondary emissions include the aqueous discharge from the methanol hydrochlorination stripper and the sulfuric and waste from the methyl chloride drying tower; however, carbon tetrachloride has not been reported as a component of these waste streams.[5]

HANDLING EMISSIONS

The following equation from reference 11 was used to develop an uncontrolled emission factor for loading of product carbon tetrachloride. Submerged loading into clean tank cars, trucks, and barges was assumed.

$$L_L = 12.46 \frac{SPM}{T}$$

L_L = Loading loss, $lb/10^3$ gal of liquid loaded

M = Molecular weight of vapors, lb/lb-mole = 154

P = True vapor pressure of liquid loading, psia

T = Bulk temperature of liquid loaded (°R)

S = A saturation factor = 0.5 for submerged file of clean tank trucks, tank cars, and barges.

For the hydrocarbon chlorinolysis, methane chlorination, and carbon disulfide processes, a bulk liquid temperature of 20°C was assumed.[1,2] Therefore:

$$T = 528°R$$

$$P = 1.73 \text{ psia}$$

$$L_L = \frac{(12.46)(0.5)(1.73)(154)}{528}$$

$$= 3.14 \text{ lb}/10^3 \text{ gal}$$

Loading loss in $lb/10^3$ gal was converted to an emission factor in terms of kg/Mg (equivalent to $lb/10^3$ lb) by dividing by the density of carbon tetrachloride (1.59 g/ml = 13.3 lb/gal)

$$\text{Emission factor} = \frac{3.14 \text{ lb}/10^3 \text{ gal}}{13.3 \text{ lb/gal}}$$

$$= 0.24 \text{ kg/Mg}$$

For the methanol hydrochlorination/methyl chloride chlorination process, the bulk liquid temperature was assumed to be 40°C.[5] Therefore:

$$T = 564°R$$

$$P = 4.08 \text{ psia}$$

$$L_L = \frac{(12.46)(0.05)(4.08)(154)}{564}$$

$$= 6.94 \text{ lb}/10^3 \text{ gal}$$

$$\text{Emission factor} = \frac{6.94 \text{ lb}/10^3 \text{ gal}}{13.3 \text{ lb/gal}}$$

$$= 0.52 \text{ kg/Mg}$$

PROCESS FUGITIVE EMISSIONS

Fugitive emissions of carbon tetrachloride and other volatile organics result from leaks in process valves, pumps, compressors, and pressure relief valves. For the chlorinolysis, hydrochlorination, and methane chlorination processes, carbon tetrachloride emission rates from process fugitive sources were based on process flow diagrams, process operation data, and fugitive source inventories for hypothetical plants,[1,2,5] and EPA emission factors for individual sources.[12]

The first step in estimating fugitive emissions of carbon tetrachloride was to list the process streams in the hypothetical plant. Their phases were then identified from the process flow diagram and their compositions are estimated. For a reactor product stream, the composition was estimated based on reaction completion data for the reactor and on the plant product slate. For a stream from a distillation column or other separator, the composition was estimated based on the composition of the input stream to the unit, the unit description, and the general description of stream of interest (ie, overheads, bottoms, or sidedraw).

After the process streams were characterized, the number of valves per stream were estimated by dividing the total number of valves at the plant equally among the process streams. Similarly, pumps were apportioned equally among liquid process streams, and relief valves were apportioned equally among all reactors, columns, and other separators. The locations of any compressors were determined from the process flow diagram.

Emissions were then calculated for pumps, compressors, valves in liquid and gas line service, and relief valves. Emissions from flanges and drains are minor in comparison with these sources and were, therefore neglected. Fugitive emissions from a particular source were assumed to have the same composition as the process fluid to which the source is exposed. For valves in liquid service, for instance, carbon tetrachloride emissions were determined by taking the product of: (1) the total number of liquid valves in carbon tetrachloride service; (2) the average carbon tetrachloride content of the streams passing through these valves; and (3) the average fugitive emission rate per valve per unit time as measured by EPA. Emissions from valves in gas service, pumps, and compressors were calculated in the same manner. For relief valves, fugitive emissions were assumed to have the composition of the overhead stream from the reactor or column served by the relief valve. Emissions from the various fugitive source types were summed to obtain total process fugitive emissions of carbon tetrachloride.

Because emissions from process fugitive sources do not depend on their size, but only on their number, total process fugitive emissions are not dependent on plant capacity. Thus, the overall emissions are expressed in terms of kilograms per hour of operation.

Hydrocarbon Chlorinolysis (Perchloroethylene CoProduct)

Hypothetical plant fugitive source inventory--[1]

800 valves
15 pumps (not including spares)
1 compressor
12 relief valves

Process Line Composition--

Of the 28 total process lines, about 9 are in carbon tetrachloride service (Figure A-1).[1] Compositons of these streams are estimated as follows:

Stream number	Phase	Composition (percent)		
		HCl	CCl_4	C_2Cl_4
1	gas		20	
3	gas	44	21	35
5	liquid		38	62
7	liquid		38	62
9	liquid		38	62
10	gas		100	
12	liquid		100	
13	liquid		100	
13a	liquid		100	

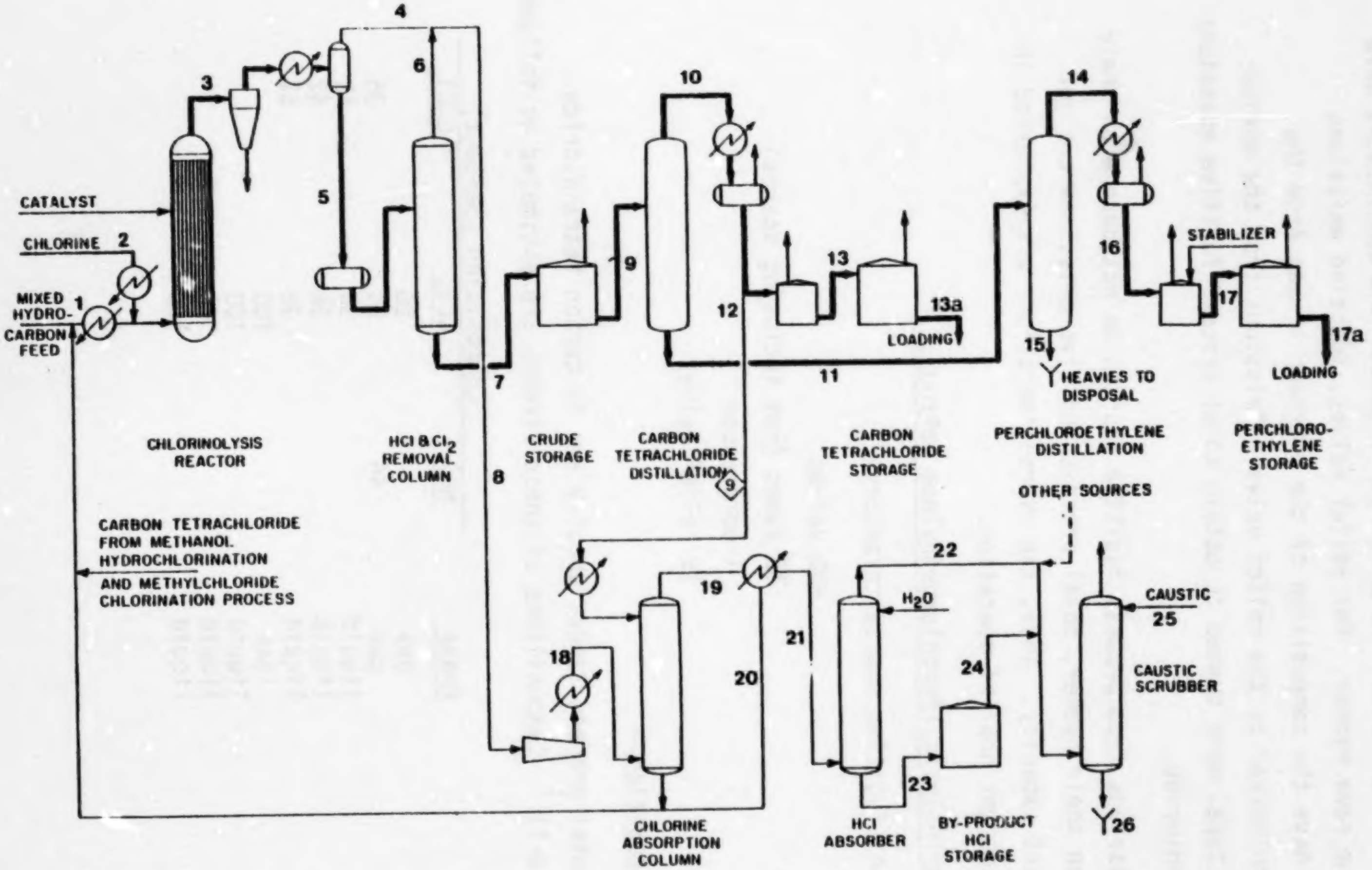

CATALYST
CHLORINE
2
MIXED HYDRO-CARBON FEED
1
3
4
5
6
7
8
9
10
11
12
13
13a
LOADING
14
15
HEAVIES TO DISPOSAL
16
STABILIZER
17
17a
LOADING
CHLORINOLYSIS REACTOR
HCl & Cl_2 REMOVAL COLUMN
CRUDE STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE STORAGE
PERCHLOROETHYLENE DISTILLATION
PERCHLORO-ETHYLENE STORAGE
OTHER SOURCES
CARBON TETRACHLORIDE FROM METHANOL HYDROCHLORINATION AND METHYLCHLORIDE CHLORINATION PROCESS
18
19
20
21
22
H_2O
23
24
CAUSTIC
25
CAUSTIC SCRUBBER
26
CHLORINE ABSORPTION COLUMN
HCl ABSORBER
BY-PRODUCT HCl STORAGE

Figure A-1. Process flow diagram for hypothetical plant using hydrocarbon chlorinolysis (perchloroethylene coproduct) process.[1]

Valves--

$$\frac{\text{800 valves}}{\text{28 lines}} \approx \text{29 valves per process line}$$

Assuming 29 valves in each of the above lines, and averaging the carbon tetrachloride contents for gas and liquid lines, total plant valve emissions were estimated as follows:

	Component emission factor (kg/hr-valve)[11]	Valves CCl_4 service	Avg composition (% CCl_4)	Emissions (kg/hr)
Liquid valves	0.0071	174	69	0.85
Gas valves	0.0056	87	47	0.23
				1.08

Pumps--

$$\frac{\text{15 pumps}}{\text{15 liquid lines}} \approx \text{1 pump per liquid process line}$$

For one pump in each of the six liquid lines in carbon tetrachloride service, an emission factor of 0.05 kg/hr/pump,[12] and average carbon tetrachloride concentration of 69 percent, pump emissions from the model plant were estimated at:

$$\text{1 pumps/line} \times \text{6 lines} \times \text{0.05 kg/hr} \times 0.69 = \text{0.21 kg/hr}$$

Compressors--

There are no compressors in carbon tetrachloride service.

Relief valves--

$$\frac{\text{12 relief valves}}{\text{7 columns}} \approx \text{2 relief valves per reactor or column}$$

The chlorinolysis reactor and carbon tetrachloride column heads will contain carbon tetrachloride at the concentrations estimated for streams 3 and 10, respectively. With an emission factor of 0.104 kg/hr/valve,[12] hypothetical plant emissions were estimated as follows:

	Number of relief valves	Emissions factor (kg/hr)	Composition (% $CHCl_3$)	Emissions (kg/hr)
Reactor	2	0.104	21	0.044
CCl_4 column	2	0.104	100	0.208
				0.252

Total process fugitive emissions--

Total process fugitive emissions for chlorinolysis hypothetical plant:

Valves-liquid	0.85
- gas	0.23
Pumps	0.21
Compressors	-
Relief valves	0.25
Total	1.54 kg/hr

Controls which can be used to reduce fugitive emissions include rupture disks on releif valves, pumps with double mechanical seals, and inspection and maintenance of pumps and valves. Double mechanical seals and rupture disks are approximately 100 percent efficient in reducing emissions from pumps and relief valves. Monthly inspection and maintenance (I/M) is about 73 percent efficient for valves in gas service, 59 percent efficient for valves in liquid service, and 61 percent efficient for pumps; while quarterly in I/M is about 64 percent efficient for gas valves, 44 percent efficient for liquid valves, and 33 percent efficient for pumps.

Overall efficiencies were calculated for three control options. The first, quarterly I/M for pumps and valves has an overall efficiency for carbon tetrachloride emissions from chlorinolysis of about 48 percent. Monthly I/M for pumps and valves has an overall efficiency of about 64 percent; and the use of double merchanical pumps, application of rupture disks to relief vavles, and monthly I/M for other valves has an overall efficiency of about 73 percent.

Methane Chlorination

Hypothetical plant fugitive source inventory[2]--

1,930 process valves
40 pumps (not including spares)
1 compressor
70 safety relief valves

Process line composition--

Of the total 50 process lines, about 18 are in carbon tetrachloride service from the chlorination reactor to carbon tetrachloride storage (see Figure A-2).[2] Compositions were estimated as follows:

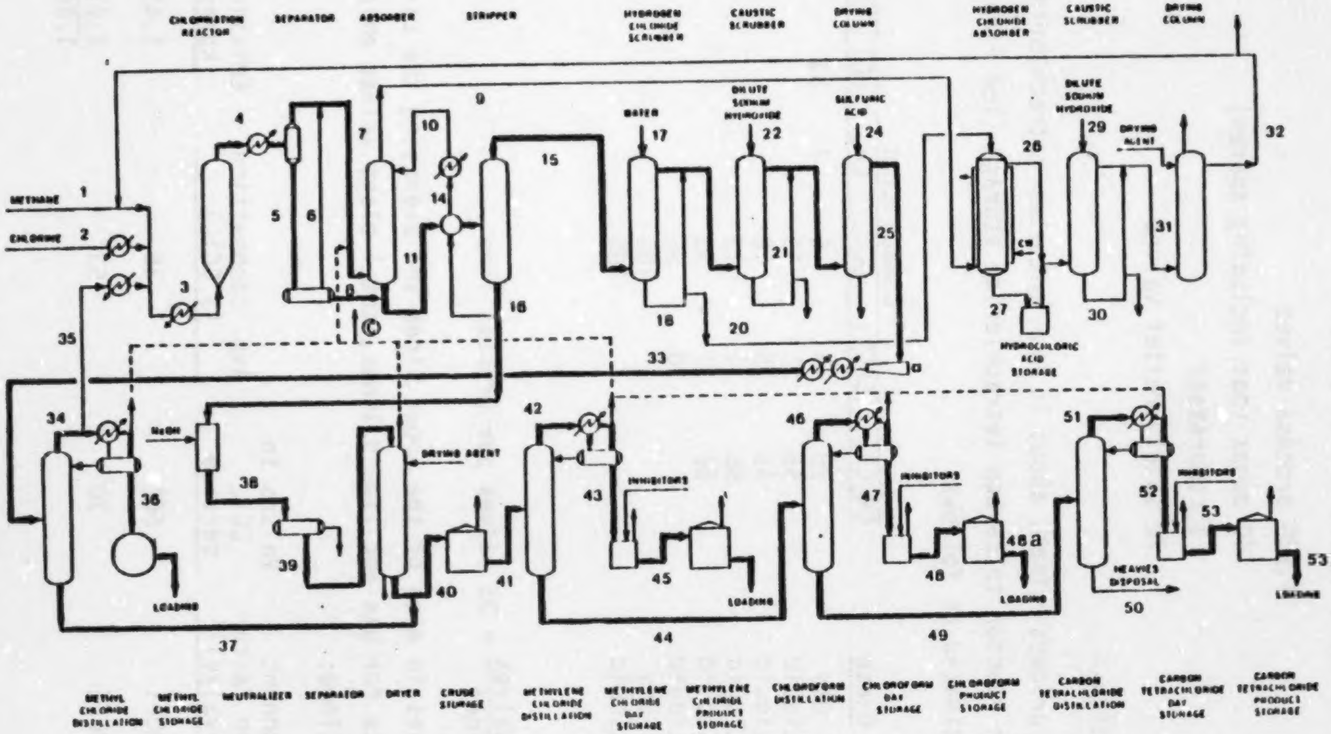
Stream number	Phase	Composition					
		CH_2Cl_2	$CHCl_3$	CCl_4	CH_4	HCl	CH_3Cl
4	Gas	28	16	6	3	33	12
5,8	Liquid	56	31	13			
11	Liquid	45	25	10			20
10,14,16	Liquid	56	31	13			
37,28,39,40,41	Liquid	56	31	13			
44	Liquid		70	30			
51	Gas			100			
49,52,53,53a	Liquid			100			

Valves--

$$\frac{1930 \text{ valves}}{55 \text{ lines}} = 35 \text{ valves per process line}$$

Assuming 35 valves in each of the above lines and averaging the carbon tetrachloride contents for gas and liquid lines, total plant valves emissions were estimated as follows:

	Component emission factor (kg/hr-valve)[11]	Valves in CCl_4 service	Avg. composition (% CCl_4)	Emissions (kg/hr)
Liquid valves	0.0071	560	36	1.43
Gas valves	0.0056	70	53	1.21
				1.64


CHLORINATION REACTOR
SEPARATOR
ABSORBER
STRIPPER
HYDROGEN CHLORIDE SCRUBBER
CAUSTIC SCRUBBER
DRYING COLUMN
HYDROGEN CHLORIDE ABSORBER
CAUSTIC SCRUBBER
DRYING COLUMN
METHANE
CHLORINE
WATER
DILUTE SODIUM HYDROXIDE
SULFURIC ACID
DILUTE SODIUM HYDROXIDE
DRYING AGENT
HYDROCHLORIC ACID STORAGE
NaOH
DRYING AGENT
INHIBITORS
INHIBITORS
INHIBITORS
HEAVIES DISPOSAL
LOADING
LOADING
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LOADING
1
2
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48a
49
50
51
52
53
53a
METHYL CHLORIDE DISTILLATION
METHYL CHLORIDE STORAGE
NEUTRALIZER
SEPARATOR
DRYER
CRUDE STORAGE
METHYLENE CHLORIDE DISTILLATION
METHYLENE CHLORIDE DAY STORAGE
METHYLENE CHLORIDE PRODUCT STORAGE
CHLOROFORM DISTILLATION
CHLOROFORM DAY STORAGE
CHLOROFORM PRODUCT STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE DAY STORAGE
CARBON TETRACHLORIDE PRODUCT STORAGE

Figure A-2. Process flow diagram for hypothetical plant using methane chlorination process.[2]

Pumps--

$$\frac{\text{40 pumps}}{\text{35 liquid lines}} \approx \text{1 pump per liquid process line}$$

Assuming and average of one pump for each of the 15 liquid process lines in carbon tetrachloride service, an emission factor of 0.05 kg/yr-pump[12] and average chloroform composition of 36 percent, pump emissions from the model plant were estimated as follows:

$$\text{1 pumps/line} \times \text{16 lines} \times \text{0.05 kg/yr} \times 0.36 = \text{0.29 kg/hr}$$

Compressors--

There are no compressors in chloroform service.

Relief valves--

$$\frac{\text{70 relief valves}}{\text{14 columns}} \approx \text{5 relief valves per column or reactor}$$

A number of column and reactor overhead streams contain carbon tetrachloride as shown below. With a relief valve emission factor of 0.104 kg/hr,[12] hypothetical plant emissions were estimated as follows:

Stream	Number of relief valves	Emission factor (kg/hr)	Composition (% $CH\,Cl_3$)	Emissions (kg/hr)
4	5	0.104	6	0.03
39	5	0.104	13	0.07
51	5	0.104	100	0.52
				0.62

Total process fugitive emission rate--

Total process fugitive emissions for methane chlorination hypothetical plant:

Valves - liquid	1.43
- gas	0.21
Pumps	0.29
Relief valves	0.62
Total	2.55 kg/hr

Controls which can be used to reduce fugitive emissions include rupture disks on relief valves, pumps with double mechanical seals, and inspection and maintenance of pumps and valves. The efficiencies of these control for individual components are described in the previous section of fugitive emissions from chlorinolysis.

Quarterly I/M for pumps and valves has an overall efficiency for carbon tetrachloride emissions from methanol hydrochlorination/methyl chloride chlorination of about 49 percent. Monthly I/M for pumps and valves has an overall efficiency of about 64 percent; and the use of double merchanical pumps, application of rupture disks to relief valves, and monthly I/M for other valves has an overall efficiency of about 75 percent.

Methanol Hydrochlorination/Methyl Chloride Chlorination

Hypothetical plant fugitive source inventory[5]--

725 process valves
15 pumps (not including spares)
2 compressors
25 safety relief valves

Process Line Composition--

Of the total 31 process lines, seven are in carbon tetrachloride service from the methyl chloride chlorination reactor to carbon tetrachlorde storage (see Figure A-3).[5] Compositons of these streams are estimated as follows:

Stream number	Phase	Composition			
		CH_2Cl_2	$CHCl_3$	CCl_4	Other
17	Gas	29	14	1.4	55
18	Liquid	29	14	1.4	55
20	Liquid	64	33	3	
24	Liquid		91	9	
25	Liquid		91	9	
26	Gas		100	-	
29	Liquid			100	
30	Liquid			100	

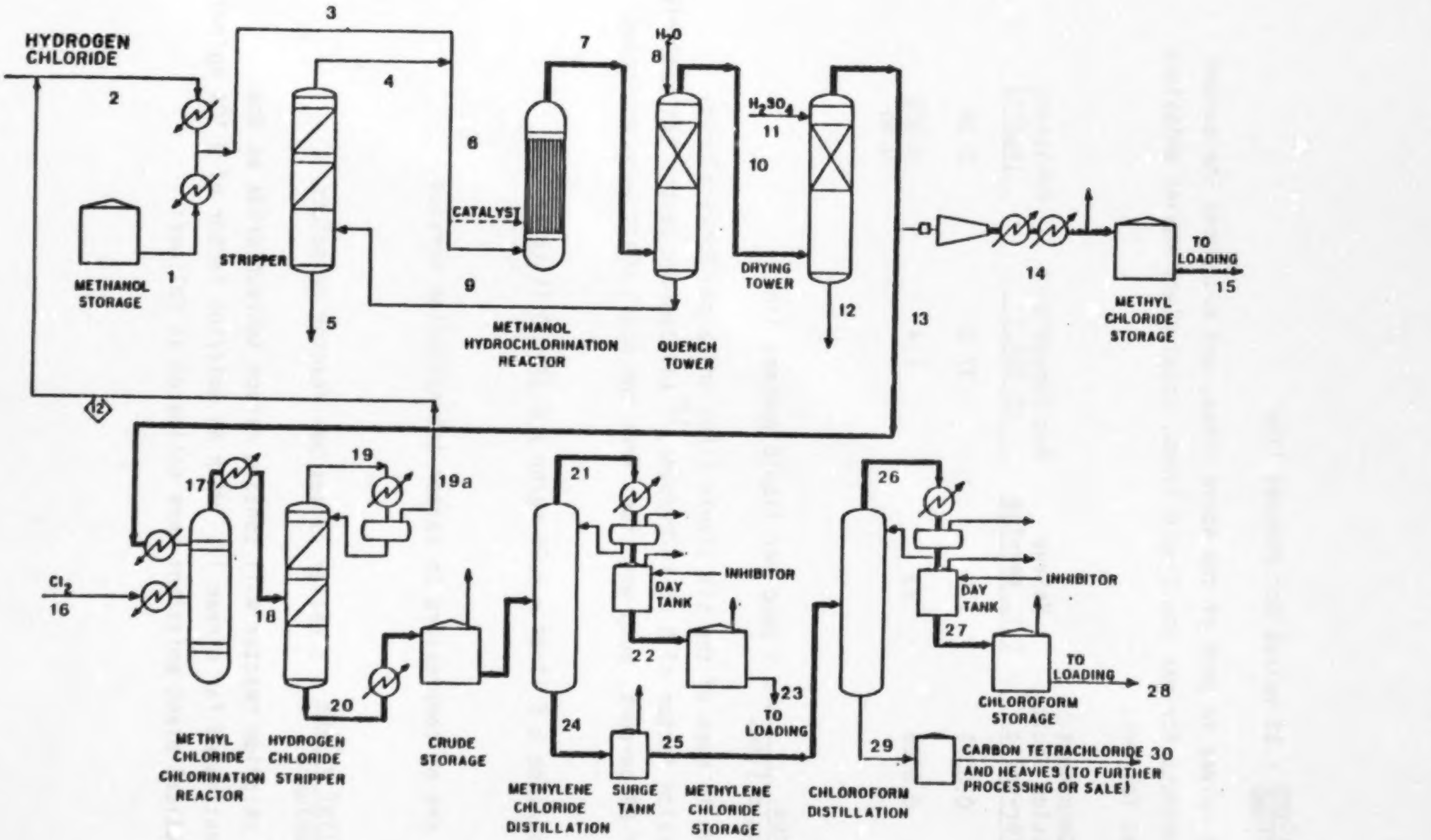
HYDROGEN CHLORIDE
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
H_2O
H_2SO_4
CATALYST
METHANOL STORAGE
STRIPPER
METHANOL HYDROCHLORINATION REACTOR
QUENCH TOWER
DRYING TOWER
TO LOADING
METHYL CHLORIDE STORAGE
12
Cl_2
16
17
18
19
19a
20
21
22
23
24
25
26
27
28
29
30
INHIBITOR
DAY TANK
INHIBITOR
DAY TANK
TO LOADING
TO LOADING
CHLOROFORM STORAGE
CARBON TETRACHLORIDE AND HEAVIES (TO FURTHER PROCESSING OR SALE)
METHYL CHLORIDE CHLORINATION REACTOR
HYDROGEN CHLORIDE STRIPPER
CRUDE STORAGE
METHYLENE CHLORIDE DISTILLATION
SURGE TANK
METHYLENE CHLORIDE STORAGE
CHLOROFORM DISTILLATION

Figure A-3. Process flow diagram for hypothetical plant using methanol hydrochlorination/ methyl chloride chlorination process.[5]

Valves--

$$\frac{725 \text{ valves}}{31 \text{ lines}} \approx 23 \text{ valves per process line}$$

Assuming 23 valves in each of the above lines, and averaging the carbon tetrachloride contents for gas and liquid lines, total plant valves emissions were estimated as follows:

	Component emission factor (kg/hr-valve)[12]	Valves CCl_4 service	Avg composition (% CCl_4)	Emissions (kg/hr)
Liquid valves	0.0071	138	37.0	0.36
Gas valves	0.0056	23	1.4	0.002
				0.36

Pumps--

$$\frac{15 \text{ pumps}}{15 \text{ liquid lines}} \approx 1 \text{ pump per liquid process line}$$

For one pump in each of the six liquid lines in carbon tetrachloride service, an emission factor of 0.05 kg/hr/pump,[12] and average carbon tetrachloride concentration of 69 percent, pump emissions from the model plant were estimated at:

1 pumps/line x 6 lines x 0.05 kg/hr x 0.37 = 0.11 kg/hr

Compressor--

There are no compressors in carbon tetrachloride service.

Relief valves--

$$\frac{25 \text{ relief valves}}{8 \text{ columns}} \approx 3 \text{ relief valves per reactor or column}$$

The methyl chloride reactor will contain carbon tetrachloride at the concentrations estimated for stream 17. With an emission factor of 0.104 kg/hr/valve,[12] hypothetical plant emissions were estimated as follows:

	Number of relief valves	Emissions factor (kg/hr)	Composition (% $CHCl_3$)	Emissions (kg/hr)
CH_3Cl reactor	3	0.104	1.4	0.0044

Total process fugitive emissions--

Total process fugitive emissions for methanol hydrochlorination/methyl chloride chlorination hypotetical plant:

Valves-liquid	0.36
- gas	0.002
Pumps	0.11
Compressors	-
Relief valves	0.004
Total	0.48 kg/hr

Controls which can be used used to reduce fugitive emissions include disks on relief valves, pumps with double mechanical seals, and inspection and maintenance of pumps and valves. The efficiencies of these controls for individual components are described in the previous section of fugitive emissions from chlorinolysis.

Overall efficiencies were calculated for three control options. The first, quarterly I/M for pumps and valves has an overall efficiency for carbon tetrachloride emissions from methanol hydrochlorination/methyl chloride chlorination of about 42 percent. Monthly I/M for pumps and valves has an overall efficiency of about 60 percent; and the use of double merchanical pumps, application of rupture disks to relief vavles, and monthly I/M for other valves has an overall efficiency of about 81 percent.

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